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STUDIES IN CATALYSIS.
IV. THE CATALYSIS OF IMIDOESTERS.

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When an imidoester decomposes in an aqueous solution, at least[1] two reactions take place; in one the ester breaks down into a nitrile and an alcohol according to

$$RC(:NH)OR \rightarrow RCN + HOR \qquad (1),$$

and in the second one, minimal decomposition is affected through the agency of water, ammonia and an acid ester resulting according to

$$RC(:NH)OR + HOH \rightarrow RCOOR + NH_3 \qquad (2).$$

The velocity of the second reaction is enormously accelerated by the addition of an acid, much in the same way that the hydrolytic decomposition of an acid ester or cane sugar is accelerated in proportion to the concentration of the hydrogen ions of the acid added. According to Prof. Stieglitz[2] the latter, so-called catalytic, actions find their explanation

[1] An acid amide is very likely another by-product. The chief product is a nitrile. *Vide* Schlesinger's later paper.

[2] Report of the Congress of Arts and Science, St. Louis, Vol. IV., p. 276 (1904); THIS JOURNAL, **39**, 29 and 402 (1908). *Vide* also Bredig: Z. Elek. Chem., **9**, 118 (1903).

simply in the formation of ionized salts of cane sugar and the esters with the added acid, in which the positive (oxonuim) ions of the organic compounds form the "active masses" which react with water; hence the action must obviously be accelerated in proportion to the increased concentration of these positive ions. These oxonium bases being so weak that exact measurements of the actual concentrations of their positive ions, under different conditions, by means of their affinity constants seemed for the time impracticable, the study of the parallel behavior of the closely related imidoesters was taken up, because all the necessary experimental data would be obtainable in this group.

At the suggestion and under the direction of Prof. Stieglitz I took up the problems of ascertaining experimentally what component in the solution of an imidoester gives rise to the decomposition expressed in (1), and especially of determining the active component in the more important reaction expressed in (2), on which the presence of an acid has a markedly accelerating effect. The second, more important reaction will be considered first.

THE ACTION OF ACIDS ON IMIDOESTERS.[1]

When an acid is added to an imidoester a condition of equilibrium is established between the weak base and its salt according to

$$RC(:NH_2Cl)OR' + H_2O \rightleftharpoons RC(:NH_2OH)OR' + HCl \quad (3).$$

The reacting constituent in the decomposition accelerated by the addition of an acid can very readily be ascertained, then, by the determination, first, of the velocity of the decomposition, and, secondly, of the concentration of each component of the system at any moment t, and by the application of the laws of chemical equilibrium and dynamics to the data obtained. The work resolved itself, then, (1) into the development of simple, rapid methods of analysis for following the velocity of the deomposition of the imidoesters by water, (2) into the determination of the hydrolysis constants in the equilib-

[1] For the theoretical and mathematical treatment of the problems reference is made to papers of Dr. Stieglitz, published in THIS JOURNAL. This paper is to deal only with the experimental work.

rium equation of the hydrolyzed salt (equation 3), that is, of the affinity constants of the imidoesters, from which the concentrations of the components of the system could be calculated, and (3) into the measurement of the velocities of decomposition of a number of imidoesters under various conditions.

The Methods of Analysis.

The simplest method of following the decomposition of a salt into ammonium chloride and an acid ester, according to

$$RC(:NH_2Cl)OR + HOH \rightarrow RCOOR + NH_4Cl \qquad (2'),$$

was suggested by the fact that the free imidoesters of the aromatic acids are oils or solids which are usually rather difficultly soluble in water but easily soluble in organic solvents like chloroform or carbon tetrachloride. The second basic ingredient in the mixture, ammonia, is, on the other hand, exceedingly soluble in water and extremely little soluble in the organic solvents. It was found, in fact, that after the addition of an alkali like sodium hydroxide the two bases could be separated quantitatively from dilute solutions by means of carbon tetrachloride, which was given the preference because of its greater density and cheapness as compared with chloroform.

Two simple methods of analysis were based on this separation. The shorter one, which was most frequently used, is as follows: If the bases are liberated from these salts in a measured portion of the mixture represented by the expression (2'), by the addition of a measured amount (v_1 cc.) of tenth-normal alkali, and the free imidoester is removed by carbon tetrachloride, the alkali is neutralized by the acid of the imidoester salt, exactly as if it were free hydrochloric acid; but with the ammonium chloride the alkali simply sets free the equivalent amount of ammonia which remains quantitatively in the aqueous solution. If, after the removal of the free ester by extraction with carbon tetrachloride, the aqueous liquid is titrated to neutrality by use of tenth-normal acid (v_2 cc.), in the presence of an indicator (methyl orange) sensitive to ammonia, the difference between the volume of the

standard alkali and acid used (v_1—v_2) represents the alkali neutralized by the acid of the ester salt. This quantity diminishes as the decomposition proceeds, ammonium chloride replacing the imido salt. In the actual work an aliquot portion (usually 25 cc.) of the solution under investigation was run into a measured excess (one and a half times the calculated amount) of tenth-normal alkali contained in a Squibb separatory funnel, the imidoester removed by three extractions with 20, 15, and 10, or 15, 10, and 5 cc. of carbon tetrachloride and the aqueous residue washed into an Erlenmeyer flask and neutralized in the presence of methyl orange. The accuracy of the method is shown by the results given in Table I., in which the weight of imidoester salt used for analysis is given in the first column, the weight of ammonium chloride mixed with the imidoester salt taken is given in the second column, and the actual volume of tenth-normal alkali used to neutralize the acid from the imidoester salt and the calculated amount required for the neutralization are listed in columns three and four, respectively. Ammonium chloride was added in the amount in which it was likely to be present in actual work in order to prove that within the limits of accuracy desired no ammonia is lost by the carbon tetrachloride extraction.

Table I.— Hydrochloride of Ethyl Imidobenzoate.[1]

Ester salt.	Ammonium chloride.	$v_1 - v_2$ used.	$v_1 - v_2$ calculated.
....	0.096	0.02	0.00
....	....	0.03	0.00
0.2313	....	12.28	12.45
....	0.070	0.22	0.00
....	0.070	0.14	0.00
0.1940	....	10.40	10.45
0.2046	....	11.05	11.07
0.2058	0.098	11.00	11.14
0.1252	0.039	6.74	6.74
0.0573	0.061	3.15	3.08
0.0409	....	2.16	2.20

The other and longer method of analysis is based on the same general principle as the one just given, but differs from it in

[1] Check analyses were made with all the imidoesters used but will not be reported. The method was always reliable for the aromatic esters.

that the imidoester base is determined directly. The imidoester was taken up from the combined carbon tetrachloride extract by shaking this with a measured excess (two or three times the calculated amount, in two successive portions) of tenth-normal sulphuric acid, and then the excess of acid neutralized by standard alkali in presence of an indicator (methyl orange or alizarinsulphonate) sensitive to the imidoester base. The carbon tetrachloride was washed with water after two extractions with the standard acid and the aqueous and acid extracts were mixed and titrated. As the imidoesters are much weaker bases than ammonia, methyl orange is not as sensitive to them as to ammonia, and the hydrochlorides of the esters react very slightly acid to methyl orange; so slightly that they produce in moderate dilutions, not strong acid tints (pink or red), but a brownish-pink color. A standard color of this tint was made for comparison and used for the end point in the titrations. For very accurate work standard tints were made for the various concentrations of salt used, since the degree of hydrolysis (equation 3) depends, of course, on the dilution. This last pre caution was rarely necessary. While the method is longer and less convenient than the first one described, it was useful especially in determining the velocities of decomposition of the imidoester salts in the presence of added excess of the imidoester base. The degree of accuracy of the method is shown by the results given in Table II. The data in the various columns have the same significance as in Table I., except that in columns three and four the volumes are of tenth-normal acid instead of alkali.

Table II.—Hydrochloride of Ethyl Imidobenzoate.

Ester salt.	Ammonium chloride.	$v_1 - v_2$ used.	$v_1 - v_2$ calculated.
0.2313	....	12.27	12.45
....	0.070	0.10	0.00
....	0.070	0.12	0.00
0.1940	....	10.42	10.45
0.2046	....	11.02	11.07
0.2058	0.099	111.10	11.14
0.1252	0.039	6.78	6.74
0.0573	0.061	3.30	3.08
0.0409	....	2.30	2.20

PREPARATION OF THE IMIDOBENZOIC ESTER HYDROCHLORIDES AND IMIDOBENZOIC ESTERS.

The Imidoester Hydrochlorides.

Particularly pure imidoester salts being desired for these determinations, their preparation by Pinner's general method, with certain modifications, will be briefly described.

According to the method of Pinner[1] they were prepared by mixing equimolecular amounts of the carefully purified and dehydrated nitrile and alcohol and saturating the mixture, at o°, with dry hydrogen chloride. The reaction

$$RCN + ROH + HCl = RC(NH_2Cl)OR \qquad (4)$$

results after a few hours' standing. By this process a very hard, crystalline mass is obtained which it is difficult to break up and still harder to free from the excess of hydrochloric acid. If, however, three or four times their volume of dry ether is added to the mixed nitrile and alcohol and the whole is then saturated with hydrogen chloride, the resulting salt is loosely, finely crystalline, easily handled and purified. The yield is not diminished, for most of the imidoester salts are quite insoluble in ether. The product was purified by filtering off the crystals and washing them with dry ether, after which the salt was kept for some time under reduced pressure in a vacuum desiccator so that all ether and free hydrochloric acid might be removed. To obtain a perfectly pure product, further processes were resorted to in special cases and will be described in those connections. These salts are thus easily prepared in quantity but are difficult to keep, since traces of moisture produce decomposition, and by long standing even the dry salt very slowly undergoes spontaneous decomposition. Two of the products of decomposition were easily shown to be ammonium chloride and benzamide by the following methods: Ammonium chloride is nearly insoluble in absolute alcohol while the imidoester hydrochlorides are freely soluble. A sample of the imidoester salt, which had stood for some time, left a considerable amount of a white, crystalline residue after the imidoester had been

[1] Pinner: The Imidoesters.

dissolved out by absolute alcohol. A portion of this white residue, after drying, gave, on analysis, 66.06 per cent chlorine instead of 66.22 per cent, the theoretical amount for ammonium chloride. The alcoholic solution was evaporated *in vacuo*. An ether extract of the crystalline residue gave a substance which melted at 125°, while benzamide melts at 128°.

The Imidobenzoic Esters.

Imidobenzoic ester hydrochlorides, when treated with alkali hydroxide in cold solutions, yield immediately the imidobenzoic ester and an alkali chloride according to this general reaction:

$$RC(NH_2Cl)OR + MOH \rightarrow RC(NH)OR + MCl + H_2O.$$

These imidoesters are colorless, highly refracting oils, or white to pale yellow solids heavier than water and little soluble in that medium, but readily soluble in alcohol and ether. The general method of preparation finally adopted was as follows, preliminary experiments having shown that the preparation of pure esters is accompanied by many difficulties. Into a separatory funnel was placed sufficient of a 5–10 per cent sodium hydroxide solution for the complete decomposition of the imidoester salt, ether was added, and the whole cooled in ice water. The cooling minimizes the decomposition of the salts. To this cold solution the solid imidoester hydrochloride was added in successive small portions while the mixture was constantly agitated to facilitate the extraction of the liberated imidoester by the ether layer. The extract was then treated with fused calcium chloride in sticks and allowed to stand for an hour or more, usually in ice water. The mixture was shaken frequently to insure drying of all parts of the ether solution. Finally the ethereal solution was siphoned from the drying agent through a dry filter into a dry flask, when the drying process was again repeated and followed by one or two more repetitions. The success of the preparation and the purity of the final product depends very much on the thorough removal of the water from the ether solution. The ether was then driven off by distillation over a water bath and the residue, if an oil, was fractionally distilled *in vacuo*;

if a solid, it was purified by recrystallization. All the esters, on standing, even in sealed tubes, decompose to a greater or less extent, and long, colorless, highly refracting, prismatic crystals separate from the liquids. In all the work where pure substances were necessary, freshly prepared esters or recently distilled portions were always used. The imido-esters were always analyzed by titrating a weighed amount, mixed with 25–30 cc. water, directly with tenth-normal acid (usually sulphuric acid) in the presence of methyl orange, that tint of red being used as the end point which was most nearly like the tint produced by a corresponding weight of the pure imido hydrochloride when dissolved in the same volume of water with the addition of an equal amount of methyl orange.

Ethyl Imidobenzoate.

Ethyl imidobenzoate was made and analyzed as described above. The following table shows the boiling points of several preparations, with the accompanying analyses. Column one shows the boiling point; two, the corresponding pressure; three, the weight of the ester taken for analysis; four, the amount of tenth-normal acid used; and column five, the calculated volume of tenth-normal acid required for the same weight of pure substance.

Boiling point.	Pressure in millimeters.	Weight of esters.	Acid used.	Acid calculated.
115°.5	....	0.2902	19.42	19.46
115°	21.5	0.4319	28.92	28.96
115°	21.5	0.4048	27.14	27.14
101°–102°	11.0	0.2402	16.13	16.10

The boiling point at 744.7 mm. pressure was 219°. The boiling in this case was accompanied by slow decomposition, as was shown by analysis of the sample.

The pure product was a colorless, somewhat viscous liquid more dense than water and having an index of refraction of 1.5278 at 20°; it is miscible in all proportions with alcohol and ether, but only very slightly soluble in water. At 25° 100 cc. of aqueous solution was found to contain 0.396 gram of ethyl imidobenzoate, or a liter will dissolve 0.026 molecule.

The ester is soluble in carbon tetrachloride and three determinations were made to find out its partition coefficient between water and carbon tetrachloride, with the following results: C_1 and C_2 indicate the amounts of imidoester dissolved in 100 cc. of each solvent, respectively, while $K = C_2/C_1$ shows the partition coefficient. The temperature was 23° (±1°).

C_1.	C_2.	C_2/C_1.
0.0194	2.450	126
0.0114	1.464	128
0.0073	0.901	123

Methyl Imidobenzoate.

This substance, prepared by the method described, was obtained pure with much greater difficulty than was experienced with any of the other esters studied, and when it was obtained pure it soon changed, so that frequent fractional distillations were necessary to prepare and keep sufficiently pure material for the work.

The following table is in every respect similar to the one given in connection with the ethyl ester. It shows the results obtained with the methyl ester.

Boiling point.	Pressure in millimeters.	Weight of ester.	Acid used.	Acid calculated.
104°	20.5	0.4000	29.46	29.60
83°	5.8	0.3554	15.67	15.64
106°	22.0	0.2724	20.05	20.15
107°	22.5	0.2680	19.80	19.83
91°.8	11.0	0.2528	18.72	18.69
....	....	0.2097	15.43	15.40
101°	18.0	0.4862	35.81	35.98
98°	14.5	0.4227	31.27	31.28
99°.7	16.5	0.4202	31.07	31.09
75°.5	3.8	0.3171	23.51	23.47

The properties of the methyl ester differ from those of the ethyl ester only in degree. It is slightly more soluble in water. The index of refraction at 20° is 1.5430. At 10.5 mm. pressure the boiling point is 10° lower than that of the ethyl ester at the same pressure.

Normalpropyl Imidobenzoate.

This ester was prepared by the general method and analyzed in the usual way. It was obtained pure more readily than any of the other esters studied. The tendency to form benzamide was much less pronounced, as indicated by the very slight amount of solid residue remaining in the flask after the distillation *in vacuo*.

Boiling point.	Pressure in millimeters.	Weight of ester.	Acid used.	Acid calculated.
121°	16	0.1836	11.25	11.25
121°.1	16	0.2757	16.97	16.90
121°	16	0.2718	16.74	16.66

The normalpropyl ester appeared to be less soluble in water than its two homologues just described, but resembled them closely in properties. The index of refraction, as determined at 20°, was 1.5173.

Isopropyl Imidobenzoate.

The isopropyl ester was prepared like the other esters. It was obtained pure with much more difficulty than its isomer and, like the methyl ester, seemed to decompose somewhat into benzamide, a residue of which was usually obtained after the fractional distillation of the ester *in vacuo*. The boiling points under the reduced pressures, together with the analytical results, are given in the table:

Boiling point.	Pressure in millimeters.	Weight of ester.	Acid used.	Acid calculated.
102°	10	0.2106	12.80	12.90
106°	13	0.2239	13.66	13.72
....	..	0.2110	12.93	12.95
114°	20	0.2127	13.05	13.04
114°	19	0.2139	13.13	13.11

The properties were the same as for the isomeric normalpropyl ester. A rough determination of solubility at room temperature (about 21°) showed that 100 cc. of solution contained 0.161 gram of the ester. The index of refraction, at 20°, was 1.5144.

Methyl Metanitroimidobenzoate.

The free ester was prepared from the hydrochloride salt by the general method. It forms a solid.

This solid was pale yellow in color and very slightly soluble in water. It melted sharply at 50°.6 and was used for the experimental work to be described later. As is shown by its conductivity in aqueous solution at 25°, it contained nothing of such a nature as would vitiate the results. This conductivity was 4×10^{-6}.

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THE AFFINITY CONSTANTS OF IMIDOESTERS BY THE CONDUCTIVITY METHOD.

The apparatus used for the work was of the kind ordinarily used in conductivity measurements; namely, a meter-wire bridge and resistance box, both of which were carefully calibrated, a specially wound induction coil, and a sensitive telephone. In some of the later work a short bridge was used. The scale on this was laid out in proportional parts. This was found sufficiently accurate for the work and much more convenient than the meter bridge. For maintaining a condition of constant temperature a large, rectangular, galvanized water bath, of about one cubic meter capacity and jacketed with asbestos, was fitted with a very large (about one liter) gas thermoregulator of the Ostwald type, filled with toluene. The water was kept thoroughly stirred by means of a four-armed, windmill-shaped stirrer run by an electric motor. After once being adjusted to 25°, this bath remained at a uniform temperature day and night for weeks, varying much less than 0°.01, as was shown by a series of observations made with a Beckmann thermometer. The level of the water in the bath was maintained constant by occasional additions so that the hydrostatic pressure exerted upon the regulator might be uniform. For the conductivity work at 18° a bath fitted up similarly to the one just described was used, except that in this case a cold water coil was essential to keep the water sufficiently cooled to enable the regulator to work.

Since the imidoester salts, when brought into water solution,

instantly begin to decompose, the ordinary method for obtaining the various concentrations, by means of successive dilutions of a concentrated solution of the substance, could not be used. Each solution investigated was made up separately by weighing the amount of salt required for 50–100 cc. of solution. This weighed amount of substance was then transferred to the dry Arrhenius cell, which had already been in the bath long enough to acquire the proper temperature, and the water for the solution, which was also at the bath temperature, was poured in. The salts are rapidly soluble, and when the electrodes were put in after the addition of the water and raised and lowered five or six times a homogeneous solution was obtained. During the time (never less than two minutes) required for the preparation of the solution, some change inevitably takes place and the first bridge reading corresponds, then, to the mixed solution of imidoester and ammonium chloride formed by the decomposition and not to the pure solution of imidoester hydrochloride, which could only be observed at zero time, a practical impossibility in this case. For getting this reading corresponding to zero time, a process of extrapolation was used. An inspection of a large number of series of measurements showed that during the first twenty or twenty-five minutes the changes in conductivity, consequently the change in bridge reading, was proportional, within the limits of experimental errors, to the time. For any given experiment, then, the exact time at which the water was poured in was noted, at the end of five minutes the first bridge reading was taken, followed by three or four more readings also at five minute intervals. From these bridge readings a simple numerical extrapolation gave the desired reading at zero time. An actual series of observations are here given to clearly illustrate this very important detail of the method. The columns in the following table have this significance: One shows the time in minutes; two, the bridge readings taken at the times given; three, the changes in bridge readings for each interval of five minutes and also the average; four, the total changes in bridge reading corresponding to each total time as calculated by means of the average difference

found from column three; and column five gives the zero-time readings of the bridge as calculated from each observed reading by adding the calculated corresponding total variations given in column four.

Time.	Bridge. Required.	Bridge difference.	Calculated total variations.	Bridge reading at zero time.
0	.....	..	..	.....
5	0.449	..	4	0.453
10	0.445	4	8	0.453
15	0.440	5	12	0.452
20	0.437	3	16	0.453
25	0.434	3	20	0.454
	Average,	4	Aver. for zero time,	0.453

The bridge reading corresponding to zero time, was, then, 0.453, and was used, together with the resistance and constant of the cell, to derive the specific conductivity of the solution at the instant of preparation. Another method by which the conductivity at zero time was obtained consisted in calculating each specific conductivity corresponding to each bridge reading and using these values in place of the bridge readings for the extrapolation calculation. This involves more calculations than the first method and, since the resulting values are nearly the same, the former method was most used.

THE HYDROLYSIS CONSTANTS FOR THE IMIDOESTER HYDROCHLORIDES.

Ethyl Imidobenzoate.

The data for the hydrolysis constant for the hydrochloride of ethyl imidobenzoate (equation 3) were determined, as described above, by Bredig's method.[1] The molecular conductivities, μ_v, for the nonhydrolyzed salt were first determined, the hydrolysis being suppressed by the addition of an excess of 0.025 and 0.0125 mole of free base. Two series of determinations were made and the results of these are summarized in Table III. Column one gives the volume in liters containing a gram molecular weight of the salt; columns two and three, the molecular conductivities, μ_v, in reciprocal

[1] Z. physik. Chem., 13, 288 (1894).

mercury units, in the presence of 0.025 and 0.0125 mole, respectively, of free base; and columns four and five, the conductivity, μ_∞, of the nonhydrolyzed salt for infinite dilution, as calculated from the previous columns by the addition of the characteristic constants, Δ_v, of Ostwald and Bredig.[1]

Table III.

	0.25 base.	0.0125 base.	0.025 base.	0.0125 base.
V.	μ_v.	μ_v.	μ_∞.	μ_∞.
32	83.4	83.2	97.4	97.2
64	86.5	87.5	97.5	98.5
128	90.3	89.5	98.3	97.5
256	92.7	92.4	98.7	98.4
		Mean,	97.97	97.90
32	83.5	83.4	97.5	97.4
64	86.1	86.9	97.1	97.9
128	89.2	89.7	97.2	97.7
256	91.7	92.7	97.7	98.7
		Mean,	97.37	97.9

The agreement in the values for μ_∞ being satisfactory, both as regards the values obtained in the presence of varying amounts of free base and as regards the duplicate series, the following mean values were considered to represent the true molecular conductivities of the nonhydrolyzed salt at 25° (±0°.01):

V	32	64	128	256
μ_v	83.4	86.7	89.6	92.4

The conductivity of the hydrochloride was next determined in the hydrolyzed solution, without the addition of any free base, and the degree of hydrolysis calculated according to

$$x = \frac{M_{obs} - \mu_v}{\mu_{HCl(v)} - \mu_v},$$

in which M_{obs}, μ_v and $\mu_{HCl(v)}$ represent the molecular conductivities of the hydrolyzed salt, the salt, and hydrochloric

[1] *Loc. cit.* In later determinations (*vide* a later paper by E. E. Barnard) a more exact graphic method was used to obtain μ_∞.

acid, respectively, all referred to the same volume, the volume containing a molecular equivalent of total electrolyte.[1] The values which were used for the molecular conductivity of hydrochloric acid at 25° were those determined by Ostwald:

V	32	64	128	256	512
μ_{HCl}	369	374	376	378	379

Table IV. summarizes the results. Column one gives the volume, in liters, containing a gram molecule of the salt; two shows the observed molecular conductivity for the hydrolyzed salt; three, the degree of hydrolysis; and column four, the hydrolysis constant calculated from

$$\frac{(1-x)V}{x^2} = \frac{k_{base}}{k_{H_2O}} = K_{hydrolysis.}$$

Table IV.

V.	$M_{obs.}$	$100x$.	$10^{-5} \times K_{hydrolysis.}$
32	85.1	0.59	9.1
32	85.1	0.58	9.5
64	89.7	1.04	5.8
64	89.4	0.94	7.2
128	93.1	1.20	8.8
256	96.3	1.36	13.0
			Mean, 8.9×10^5

The affinity constant for ethyl imidobenzoate is then:

$$K_{aff.} = K_{hydrolysis} \times K_{H_2O} = 8.9 \times 10^5 \times 1.2 \times 10^{-14} = 1.1 \times 10^{-8}.$$

Methyl Imidobenzoate.

The experimental results for the determination of the constant for the hydrochloride of methyl imidobenzoate are given in Tables V. and VI. Table V. gives the data for the determination of the molecular conductivity of the nonhydrolyzed salt at various dilutions and the columns have the same significance as in Table III.

[1] Stieglitz and Derby: THIS JOURNAL, 31, 449 (1904).

Table V.

	0.25 base.	0.0125 base.	0.025 base.	0.0125 base.
V.	μ_v.	μ_v.	μ_∞	μ_∞
32	....	85.3	....	99.3
64	89.3	89.9	100.3	100.9
128	91.5	92.1	99.5	100.1
256	....	95.0	....	101.0
		Mean,	99.9	100.7
32	....	86.7	....	100.7
64	89.9	90.7	100.9	101.7
128	92.7	92.9	100.7	100.9
256	....	94.3	....	100.3
		Mean,	100.8	100.8

The mean of all of the values for the conductivity at infinite dilution was 100.5. The following values were taken as representing the molecular conductivities of the nonhydrolyzed salt:

V	32	64	128	256	512
μ_v	86.5	89.5	92.5	94.5	96.5

Following are the graphically interpolated values for intermediate dilutions corresponding to the four odd dilutions listed in Table VI.:

V	29.4	58.8	117.6	235.2
μ_v	86.1	89.0	91.8	94.2

Table VI. gives the observed conductivities of the hydrolyzed salt. The columns have the same significance as in Table IV.

Table VI.

V.	$M_{obs.}$	$100x$.	$10^{-5} \times K_{hydrolysis.}$
32.0	89.7	1.13	2.47
32.0	89.7	1.13	2.47
32.0	89.5	1.05	2.87
64.0	93.6	1.44	3.04
64.0	93.8	1.47	2.91
64.0	93.6	1.44	3.04
58.8	92.3	1.16	4.32
128.0	97.8	1.87	3.59
128.0	96.6	1.80	3.88
128.0	97.8	1.87	3.59
128.0	97.5	1.76	4.06

Table VI—(Continued).

v.	$M_{obs.}$	$100x$.	$10^{-5} \times K_{hydrolysis.}$
117.6	97.4	1.97	2.97
256.0	101.0	2.29	4.77
256.0	99.9	1.90	6.94
256.0	100.9	2.25	4.94
235.2	100.8	2.33	4.23
512.0	104.2	2.70	6.83

Mean, 3.93×10^5

The affinity constant for methyl imidobenzoate, as calculated from the hydrolysis constant, is 4.7×10^{-9}.

n-Propyl Imidobenzoate.

The following tables give the data for determining the hydrolysis constant of the *n*-propyl imidobenzoate. The significance of the columns is the same as in Tables III. and V. The amount of free base present was sufficient to suppress the hydrolysis but was not accurately weighed out in each case, as was done in the determinations on the ethyl and methyl esters. The values for μ_∞ were obtained by graphic interpolation.

Table VII.

v.	μ_v.	μ_∞.	v.	μ_v.	μ_∞.
32	82.4	96.4	128	88.1	96.1
48	84.0	96.2	192	89.1	95.9
64	85.4	96.4	256	91.1	97.1
96	87.3	96.5	384	91.6	96.0

Mean, 96.3

Table VIII. gives the degree of hydrolysis and the value of the constant. The columns have the same significance as in Tables IV. and VI.

Table VIII.

v.	$M_{obs.}$	$100x$.	$10^{-5} \times K_{hydrolysis.}$
32	83.6	0.42	18.1
48	86.0	0.69	10.0
64	88.0	0.90	7.8
96	89.6	0.80	14.9
128	91.5	1.18	9.1
192	92.3	1.11	7.4
256	94.9	1.32	14.5

Mean, 12.8×10^5

The affinity constant, as calculated from the hydrolysis constant, is 15.4×10^{-9}.

Isopropyl Imidobenzoate.

Tables IX. and X. give the results of the conductivity measurements for isopropyl imidobenzoate, the degree of hydrolysis, and the value of the hydrolysis constant:

Table IX.

$V.$	$\mu_v.$	$\mu_\infty.$	$V.$	$\mu_v.$	$\mu_\infty.$
32	82.0	96.0	256	90.1	96.1
64	85.4	96.4	512	91.7	95.7
128	88.1	96.1	407.3	91.5	96.2
				Mean,	96.08

Table X.

$V.$	$M_{obs.}$	$100\,x.$	$10^{-5} \times K_{hydrolysis.}$
32	83.6	0.56	10
32	84.2	0.76	6
64	87.3	0.65	16
128	90.6	0.86	17
256	93.0	1.00	25
256	93.8	1.28	15
512	96.5	1.66	18
407.3	96.2	1.63	15
			Mean, 15×10^5

The value of the affinity constant, as calculated from the hydrolysis constant, is 1.8×10^{-8}.

Methyl Metanitroimidobenzoate.

Because of the great rapidity of decomposition of this body, the conductivity determinations were carried out at a temperature of 18°. The free methyl metanitroimidobenzoate base was found to be much less soluble than any of those previously studied and, for the determination of the conductivities of the nonhydrolyzed salt, a sufficient quantity of base was added to each solution so that a little remained undissolved after the thorough mixing preceding the measurements. To be absolutely sure that all hydrolysis was suppressed, each solution was tested with methyl orange at the end of the observations and proven to be a little alkaline in reaction.

Table XI.

V.	μ_v.	Δ^1.	μ_∞.
32	73.8	12.1	85.9
32	73.8	12.1	85.9
48	75.6	10.4	86.0
64	76.4	9.6	86.0
96	78.0	7.8	85.8
128	78.8	7.0	85.8
192	80.4	5.8	86.2
256	80.5	5.2	85.7
256	81.1	5.2	86.3
		Mean,	85.96

Table XII.

V.	$M_{obs.}$	$100\,x$.	$10^{-4} \times K_{hydrolysis.}$
32	79.25	2.10	7.1
48	82.83	2.77	6.1
64	84.85	3.20	6.1
96	88.84	4.12	5.4
128	91.70	4.91	5.1
192	94.73	5.45	6.1
256	99.30	7.16	4.6
		Mean,	5.8×10^4

The affinity constant[2] is then 3.7×10^{-10}.

The Affinity Constant of Ethyl Imidobenzoate Determined by a Colorimetric Method.

The determination consisted in simply taking equal volumes of water solutions of the hydrochloride of known concentration, placing them in color-comparison tubes with the same amounts of methyl orange, and adding standard acid to the water until the red tint matched the red of the salt solution employed. Knowing the volume of the water and the amount of standard acid used and the concentration of the imidoester hydrochloride, a simple calculation gave the amount of free acid formed by hydrolysis and the degree of hydrolysis. The following table, XIII., gives the results. Column one

[1] Bredig's differences refer to 25° C. A temperature correction of 0.019 per degree was used.

[2] K_{H_2O} was taken as 0.64×10^{-14} at 18°, according to Arrhenius: "Lehrbuch der Elektrochemie," p. 186.

gives the volume containing a gram molecule of the salt; two, the percentage of hydrolysis; and column three, the hydrolysis constant as calculated by the equation previously used.

Table XIII.

V.	100 *x*.	$10^{-5} \times K_{hydrolysis}$.	*V.*	100 *x*.	$10^{-5} \times K_{hydrolysis}$.
32	0.46	15	64.0	0.66	15
(32)	(0.36)	(25)	95.6	0.75	17
32	0.43	17	95.6	0.82	12
64	0.72	12	191.3	1.27	12
64	0.61	17	382.6	2.00	10

Mean, 14×10^5

Mean by conductivity, 9.1×10^5.

The Velocity of Decomposition of the Hydrochlorides of Imidobenzoates.

In order to determine the reacting substance in the decomposition of an imidoester by water into an ester and ammonia (equation 2 or 2′), and to establish rigorously the cause of the acceleration of the decomposition by the addition of an acid, the velocity of the change of methyl imidobenzoate, in the presence of hydrochloric acid, was determined under varying conditions, at a temperature of 25° (+0°.01), and the experimental data subjected to analysis. In most of the experiments the hydrochloride of the imidoester was used alone; in other cases the experiments were carried out with an excess of the free base present with the hydrochloride. In either case, we have simultaneously two reactions taking place, with still a third reaction, according to equation (1), which is exceedingly slow and ordinarily negligible, but which was, nevertheless, taken into account, as previously described.[1] A condition of equilibrium is established between the salt, base, acid, and water according to equation (3), which is continuously disturbed by the water decomposing one of the constituents of the system into ammonium chloride and acid ester (equation 2′); the condition of equilibrium in (3) may be said to establish itself at each instant in conformity to the

[1] Stieglitz: *Loc. cit.*

changing conditions, since only direct, simple ionic reactions are involved; consequently, we have at every moment, according to Walker[1] and Arrhenius,[2] for the hydrolyzed salt solution, an equilibrium according to equation (3):

$$C_{salt} = K_{hydrolysis} \times C_{base} \times C_{acid}.$$

In the second place, the decomposition is proceeding with a measurable velocity, either the total substance, the salt and base indifferently, or only the free base or the salt (*i. e.*, its positive ions in the dilute solution used) reacting with water to give the products of the action represented in equation (2).[3]

The first possibility that the total substance, base and salt indifferently, enter into action with the water, may be taken to illustrate the principle of an acceleration produced by the acid present, an acceleration not due to the salt formation, which, of course, inevitably follows, but, in some mysterious way, to the mere presence of the acid in the system. For this case we have a monomolecular reaction proceeding with a velocity proportional to the total substance present.

$$\frac{dx}{dt} = k_{subst} \times C_{subst}. \qquad (5),^4$$

$$k_{subst} = \frac{1}{t_2 - t_1} \log \text{nat} \frac{C - x_1}{C - x_2} \qquad (6).$$

The reliability of such an interpretation is best ascertained by applying the equation to the data obtained for velocity determinations, in which an excess of free base is added to the salt solution. The degree of hydrolysis, when the salt is used alone, being exceedingly small (see $100x$ in Tables IV., VI., etc.), the total substance is almost the same as the salt content. Column seven, Table XIV., gives the values for $k_{subst.}$ calculated under these conditions according to (6), and a comparison of experiment four, in which no excess of free base was present, with experiment five, where an ex-

[1] Z. physik. Chem., **4**, 319 (1889).
[2] *Ibid.*, **5**, 17 (1890).
[3] Stieglitz: *Loc. cit.*
[4] $C_{subst.}$ is a function of x.

cess of free base was used, shows that $k_{subst.}$ is no true constant.

The second possibility,

$$\frac{dx}{dt} = k_{base} \times C_{base}'$$

that the free base present in the hydrolyzed solution is the active substance present, represents another possibility of an enhanced reactivity, not due to salt formation simply, but to some other undiscovered property of the hydrochloric acid.[1] The analysis of this case is more complicated than the previous one. Stieglitz finds for this case that we would have

$$k_{base} = \frac{1}{K_v (t_2 - t_1)} \left[\sqrt{R - 4K_v x_1} - \sqrt{R - 4K_v x_2} + (1 - s - K_v) \log \text{nat} \frac{\sqrt{R - 4K_v x_2} + (1 - s - K_v)}{\sqrt{R - 4K_v x_1} + (1 - s - K_v)} \right] (7),$$

in which $R = (1 - s + k_v)^2 + 4K_v s$ and the total original concentration of the imidoester used, both as salt and as free base, is called one gram molecule in V liters, the known original concentration of the salt (the added acid) s gram molecules in V liters, and x_1 and x_2, the parts of a gram molecule in V liters decomposed in t_1 and t_2 minutes, respectively. For a given experiment V is a given number and K_v is used for $V/K_{hydrolysis}'$ the latter being the hydrolysis constant of equation (3) as established by Tables IV., VI., etc. When no excess of free base is used ($s = 1$), the base present in the solution results entirely from the hydrolysis of the hydrochloride and we may calculate k_{base} from

$$k_{base} = \frac{2}{(t_2 - t_1)\sqrt{K_v}} \left[\sqrt{1 - x_1} - \sqrt{1 - x_2} \right] (8).^2$$

A few calculations of k_{base}', made according to (7) and (8), are given in column six, Table XIV., and comparison of the values of k_{base} in experiments three and five, in which excess of free base was absent and present, respectively, shows that k_{base} is as little a true constant as $k_{subst.}$

[1] See Stieglitz: THIS JOURNAL, **39**, 402, in which such theories are critically considered.

[2] Stieglitz: *Loc. cit.*

In the third possibilty considered, the fact that addition of an acid accelerates the decomposition of an imidoester and at the same time forms its salt made it extremely probable, according to Stieglitz, that the reacting substance in equation (2) would be found to be rigorously the salt (the positive ions, in the dilute solutions used), in which case the reaction velocity would be accelerated simply in proportion to the increased concentration of the salt. For this case

$$\frac{dx}{dt} = k_{salt} \times C_{salt} \qquad (9)^1,$$

and we have:

$$k_{salt} = \frac{1}{t_2 - t_1}\left[\frac{1 - s + K_v}{1 - s} \log \text{nat} \frac{\sqrt{R - 4K_v x_1} - (1 - s + K_v)}{\sqrt{R - 4K_v x_2} - (1 - s + K_v)} + \frac{1 - s - K_v}{1 - s} \log \text{nat} \frac{\sqrt{R - 4K_v x_1} + (1 - s - K_v)}{\sqrt{R - 4K_v x_2} + (1 - s - K_v)}\right] (10),^2$$

or, considering only the values affecting the significant numbers in the result, we have the simpler expression:

$$k_{salt} = \frac{1}{t_2 - t_1} \log \text{nat} \frac{\sqrt{R - 4K_v x_1} - (1 - s + K_v)}{\sqrt{R - 4K_v x_2} - (1 - s + K_v)} \quad (10'),$$

in which the symbols have the same significance as in (7). When $s = 1$, as is the case when no free base is added, we have

$$k_{salt} = \frac{1}{t_2 - t_1}\left[\log \text{nat} \frac{1 - x_1 - \sqrt{(1 - x_1)\,K_v}}{1 - x_2 - \sqrt{(1 - x_2)\,K_v}} - \sqrt{\frac{K_v}{1 - x_1}} + \sqrt{\frac{K_v}{1 - x_2}}\right] (11).$$

For less rigorous calculations, when $s = 1$, the salt being very little hydrolyzed, we may use the simple logarithmic form, for determining k_{salt}, with a sufficient degree of accuracy:

$$k_{salt} = \frac{1}{t_2 - t_1} \log \text{nat} \frac{C - x_1}{C - x_2} \qquad (12).$$

The analysis of the experimental data as given in Table XIV., column five, shows that constant values for k_{salt} are obtained, regardless of the varying conditions used.

[1] C_{salt} is a function of x.

[2] Stieglitz: *Loc. cit.*

Ethyl Imidobenzoate.

The results obtained for ethyl imidobenzoate at 25° are given in Table XIV. In later tables the influences of added electrolytes (excess of acid) on the velocity of the reaction will be given, as well as the reaction velocities at lower temperatures than 25°.

In column one of the table are given the conditions of the experiment, the volume V containing one gram molecule of the total substance (free base and salt), s representing the proportion of salt used, and v the volume of solution taken for each titration. Column two gives the time in minutes; three, the cubic centimeters of tenth-normal alkali neutralized by the imidoester salt (see p. 439); four gives the percentage of substance decomposed in time t. In column five is given the constant for k_{salt} as calculated by means of equation (10), or, in the absence of an excess of free base, from (11) or (12). Column six shows the values of k_{base} as calculated by means of equation (7), while column seven gives the constant for k_{subst} as calculated with common logarithms according to equation (6).

Table XIV.—Ethyl Imidobenzoate at 25°.

	t.	v.	$100x$.	$10^5\, k_{salt}$.	k_{base}.	$43430\, k_{subst}$.
1.	0	11.99	5.03	...	....	....
$V = 20$	60	9.94	21.27	313	....	....
$s = 1$	120	8.26	34.58	312	....	....
	180	6.81	46.06	316	....	....
$v = 25$	620	1.64	87.00	323	....	....
	Mean: $k_{salt} = 0.00316$				....	....
2.	0	12.21	3.30	...	....	....
$V = 20$	60	10.14	19.69	310	....	....
$s = 1$	110	8.61	31.81	320	....	....
$v = 25$	300	4.85	61.59	310	....	....
	Mean: $k_{salt} = 0.00313$				....	....
3.	0	12.50	0.0	...	....	....
	5	12.18	2.56	...	....	....
$V = 20$	40	10.95	12.40	306	0.62	....
$s = 1$	80	9.71	22.32	304	0.60	....
$v = 25$	180	7.14	42.88	308	0.56	....
	300	4.96	60.32	306	0.51	...
	540	2.38	80.96	308	0.44	....
	Mean: $k_{salt} = 0.00306$					

Table XIV—(Continued).

	t.	*v.*	100 *x.*	$10^5 k_{salt}$.	k_{base}.	43430k_{subst}.
4.	(10)	(9.76)	(2.40)	...	....	...
	60	8.56	14.40	(262)	....	...
V = 10	120	7.11	28.90	310	....	134
s = 1	210	5.45	45.50	304	....	131
v = 10	270	4.55	54.50	304	....	131
	330	3.78	62.20	306	....	132
	450	2.62	73.80	306	....	132
	570	2.08	79.20	(276)	....	...

Mean: k_{salt} = 0.00306

5.	0	12.50	0.0	...	....	..
	10	12.18	2.56	...	....	..
V = 20	70	10.64	14.88	287	0.0084	98
s = 0.75	160	8.74	30.08	299	0.0074	96
v = 25	250	7.26	41.92	305	0.0063	94

Mean: k_{salt} = 0.00297

The grand average for k_{salt} is 0.00307.

Methyl Imidobenzoate.

The following table gives the data and the constants calculated for methyl imidobenzoate. As for the ethyl ester, K_{salt} is the only real constant under all conditions.

Table XV.—Methyl Imidobenzoate at 25°.

	t.	*v.*	100 *x.*	$10^5 k_{salt}$.	k_{base}.	43430k_{subst}.
1.	0	(10.05)	(20.4)	...	....	....
	60	8.76	30.62	...	....	....
V = 20	120	6.22	50.74	573	....	....
s = 1	180	4.44	64.83	568	....	....
v = 25	300	2.25	82.18	568	....	....

Mean: k_{salt} = 0.00570

2.	0	11.09	11.28	...	....	...
V = 40	40	8.51	31.92	...	....	...
s = 1	100	6.07	51.44	571	....	245
v = 50	170	4.06	67.52	577	....	247
	210	3.24	74.08	576	....	247
	270	2.31	81.52	576	....	246
	330	1.63	86.96	580	....	247
	390	1.16	90.72	580	....	248

Mean: k_{salt} = 0.00577

Table XV—(Continued).

	t.	v.	$100x$.	$10^5 k_{salt}$.	k_{base}.	$43430 k_{subst}$.	
3.	0	(12.50)	.....	...	....	....	
	25	10.83	13.36	...	....	....	
$V = 20$	65	8.67	30.64	560	....	....	
$s = 1$	110	6.68	46.56	573	....	....	
$v = 25$[1]	170	4.96	60.32	543	....	....	
	260	3.18	74.56	530	....	....	
	350	2.04	83.68	520	....	....	
	440	1.18	90.56	541	....	....	

Mean: $k_{salt} = 0.00545$

4.	0	(12.50)	....	...	....	...	
	10	11.80	5.60	...	....	...	
$V = 20$	40	9.89	20.88	(592)	0.771	(256)	
$s = 1$	85	7.83	37.36	551	0.680	238	
$v = 25$[2]	130	6.15	50.80	548	....	236	
	220	3.83	69.36	541	0.560	233	
	310	2.31	81.52	550	....	236	
	400	1.42	88.64	550	0.430	235	

Mean: $k_{salt} = 0.00548$

5.[3]	0	15.95	....	...	....	...	
	5	15.38	3.57	...	....	...	
$V = 15.7$	45	12.77	19.94	603	0.0195	202	
$s = 0.784$	85	10.96	31.28	552	0.0165	184	
$v = 25$	125	9.28	41.81	608	0.0151	183	
	165	8.17	48.77	584	0.0129	172	

Mean: $k_{salt} = 0.00587$

[1] $v = 50$ cc. for the seventh titration.

[2] $v = 50$ cc. for the sixth and seventh titrations.

[3] Taking into account the simultaneous very slow decomposition of the free base present into benzonitrile and methyl alcohol, according to the velocity constant as determined (see p. 86), we find for k_{salt} according to Stieglitz (*loc. cit.*):

t	45	85	125	165
$10^5 k_{salt}$	593	543	596	571

Mean: $k_{salt} = 0.00576$

Table XV—(Continued).

		t.	v.	100 x.	$10^5 k_{salt}$.	k_{base}.	$43430 k_{subst}$.
6[1].		0	12.50	...	...	....	...
		20	11.10	11.20	...	....	...
		60	9.35	25.20	540	0.0201	186
V =	20	115	7.49	40.08	568	0.0160	180
s =	0.8	205	5.40	56.08	568	....	170
v =	25	255	4.60	63.20	603	0.0707	162
		310	3.86	69.12	548	....	157

Mean: k_{salt} = 0.00565

Grand average: k_{salt} = 0.00562.

n-Propyl Imidobenzoate.

The next table gives the data for *n*-propyl imidobenzoate hydrochloride as determined and calculated for a temperature of 25°. The columns have the same significance as in the tables for the other esters.

Table XVI.—n-Propyl Imidobenzoate at 25°.

		t.	v.	100 x.	$10^5 k_{salt}$.
		0	11.98	...	...
V =	20	20	11.21	5.73	297
		80	9.40	20.95	295
s =	1	140	7.89	33.64	294
		200	6.59	44.74	304
v =	25	260	5.59	52.99	292
		325	4.57	61.57	295
		380	3.88	67.37	290

Mean: k_{salt} = 0.00295

Methyl Metanitroimidobenzoate.

The next table gives the data for the decomposition velocity of methyl metanitroimidobenzoate and shows the constants obtained. Owing to the very rapid rate of change of this substance, accurate measurements at 25° were impossible and the experiments were therefore conducted at 18°.

[1] Allowing, as in (3), for the slow decomposition of the base, we have:

t	60	115	205	255
$10^5 k_{salt}$	540	558	571	580

Mean: k_{salt} = 0.00562

Table XVII.—Methyl Metanitroimidobenzoate at 18°.

	t.	*v.*	100 *x.*	$10^4 k_{salt}$.	k_{base}.	$4343\, k_{subst.}$
1.	0	10.43	0.0	...	...	...
	11	7.91	24.14	256	...	109
	23	5.87	43.72	255	...	109
$V = 20$	35	4.33	58.47	257	...	109
$s = 1$	48	3.22	69.12	252	...	106
$v = 25$	63	2.28	78.14	249	...	105
	76	1.71	83.60	247	...	103
	88	1.27	87.82	248	...	104
	101	0.95	90.89	246	...	103
			Mean: $k_{salt} = 0.0251$			
2.	0	.....	.....	...	...	...
	6	10.71	13.02	...	...	...
$V = 18.2$	17	7.99	32.80	258	0.194	102
$s = 0.909$	28	6.04	46.98	255	...	98
$v = 25$	39	4.52	58.04	256	0.146	96
	51	3.31	66.84	257	...	93
	62	2.51	72.65	255	...	90
	73	1.85	77.45	259	0.104	87
			Mean: $k_{salt} = 0.0257$			
3.	0	10.78	0.0	...	...	...
$V = 40$	14	7.58	29.69	251	...	109
$s = 1$	27	5.54	48.61	254	...	107
$v = 50$	40	4.14	61.59	248	...	104
	52	2.95	72.64	258	...	108
	66	2.18	79.78	245	...	105
	78	1.66	80.61	(219)	...	104
	97	1.28	88.12	(230)	...	102
	103	0.95	90.10	(236)	...	103
			Mean: $k_{salt} = 0.0251$			

The Effect of an Excess of Hydrochloric Acid on the Velocity of Decomposition of the Imidobenzoate Esters.

The velocity of decomposition of the hydrochloride of methyl imidobenzoate into ammonium chloride and methyl benzoate was determined at 25° in the presence of excess of hydrochloric acid varying in amount from 0.05 to 0.5 mole, the salt solution being 0.05 molar. The experimental results are given below, and the conclusions based upon them follow the table. The velocity constant was calculated according to equation (12).

Table XVIII.—Methyl Imidobenzoate.

t.	*v.*	43430*k*.
1. 0.05 salt, 0 acid.		
0	11.80	....
30	9.89	(256)
75	7.83	237
120	6.15	236
210	3.83	233
300	2.31	236
390	1.42	235
	Mean,	235
3. 0.05 salt, 0.05 acid.		
0	12.19	...
40	9.78	239
80	7.81	241
120	6.26	241
220	3.81	230
	Mean,	238
5. 0.05 salt, 0.10 acid.		
0	12.00	...
40	9.95	(203)
80	8.00	220
120	6.28	234
160	5.25	224
240	3.56	220
320	2.48	214
	Mean,	222
7. 0.05 salt, 0.15 acid.		
0	11.53	...
35	9.50	(240)
75	8.18	199
115	6.70	205
155	5.33	216
235	3.70	210
315	2.24	226
395	1.56	220
	Mean,	213
9. 0.05 salt, 0.50 acid.		
0	11.88	...
35	10.27	181
75	8.45	197
115	6.98	201
155	6.04	190
195	4.97	194
	Mean,	193

t.	*v.*	43430*k*.
2. 0.05 salt, 0 acid.		
0	10.83	...
40	8.68	240
85	6.68	(247)
145	4.96	234
235	3.18	227
325	2.04	(223)
415	1.18	232
	Mean,	234
4. 0.05 salt, 0.05 acid.		
0	10.79	...
40	8.88	(212)
85	6.82	235
120	5.64	236
185	4.00	233
	Mean,	235
6. 0.05 salt, 0.10 acid.		
0	(10.36)	...
40	8.82	...
120	5.73	234
180	4.21	229
260	2.97	215
340	1.81	229
420	1.16	232
	Mean,	228
8. 0.05 salt, 0.50 acid.		
0	11.15	...
40	9.35	191
80	7.86	190
120	6.47	197
160	5.55	189
240	3.88	191
300	3.01	190
360	2.47	182
	Mean,	190

Table XIX.—Ethyl Imidobenzoate.

t.	*v.*	$10^5 k_{salt}$.	*t.*	*v.*	$10^5 k_{salt}$.
1. 0.05 salt, 0 acid.			2. 0.10 salt, 0.10 acid.		
0	12.19	...	0	8.56	...
35	11.12	(262)	60	7.11	309
75	9.75	298	150	5.45	301
175	7.16	305	210	4.55	301
295	4.95	305	270	3.78	303
535	2.38	305	290	2.62	303
	Mean,	303		Mean,	303
3. 0.05 salt, 1 acid.			...	...	...
0	11.91	...	...	...	...
45	10.84	209	...	...	...
105	9.67	198	...	...	...
185	8.19	202	...	...	...
295	6.55	203	...	...	...
405	5.17	206	...	...	...
	Mean,	204			

According to the theory of Stieglitz,[1] the decomposition of imidoesters by water is caused by the action of the ions of water on the positive ions of the imidoester, according to

$$RC(:\overset{+}{N}H_2)OR + HOH \rightarrow RCO_2R + \overset{+}{N}H_4 \qquad (13).$$

Now, in the first place, an addition of an excess of hydrochloric acid must produce a depression of the degree of ionization of the imidoester salt, the salt ionizing in a mixture of electrolytes according to the concentration of the total electrolyte present. On the basis of the principle of isohydric solutions that solutions containing a positive or negative ion in common in the same concentration do not affect each other's ionization, one can imagine, with Arrhenius, for each of the above mixtures, the solvent so divided between the salt and the acid that solutions of like concentration of chlorine ions result, and the degree of ionization of the salt and acid in the resulting mixture may be calculated. For these calculations Schlesinger's[2] data on the degrees of ionization of the hydrochloride of methyl imidobenzoate were used, and allow-

[1] *Loc. cit.*

[2] See a later report by Schlesinger in THIS JOURNAL.

ance was made for the greater degree of ionization of the hydrochloric acid, which results in the acid receiving a larger share of the water than would correspond to the molecular proportions. Table XX., page 469, gives in column one the excess of acid actually used and in column two the molecular concentration of the salt, *whose degree of ionization in pure aqueous solution would correspond to that of the salt in the mixture.* Column three gives the degree of ionization of the salt corresponding to these concentrations, and column four, the degree of ionization of the acid for the mixture. The interpolations necessary were made rectilinearly from the experimental values for the nearest molecular concentrations. It was not considered important to make more exact interpolations in this series, since the relations are being more rigorously investigated in this laboratory.[1] Column five shows the mean observed velocity constants, referred to the total salt, as obtained from Table XVIII., and column six gives the velocity constant referred only to the positive ion of the salt, k_{salt} being divided by α_{salt}.

In the second place, the addition of an excess of hydrochloric acid will have a so-called "salt-effect" on the decomposition of the imidoester salt by water,[2] as it has in other changes in which water acts, such as the catalysis of esters or of cane-sugars,[3] the "salt-effect" probably consisting, in this case, in an increase of the degree of the ionization of water, that is, it probably affects the concentrations of the reacting ions of water in the reaction expressed by equation (13). This "salt-effect" is most likely produced only by the ionized portion of the acids and salts, as suggested by Arrhenius, and as results obtained in this laboratory uniformly confirm. In the experiments under consideration, after allowing for the effect of the change of the degree of ionization of the imidoester salt, it will be noted (Table XX., column 6) that 43430 k/α rises from 275 for the 0.05 salt, without any excess of acid, to 400 for an excess of 0.5 mole of acid—that

[1] *Vide* a later article by E. E. Barnard.

[2] Stieglitz: THIS JOURNAL, **39**, 166.

[3] Arrhenius: Z. physik. Chem., **1**, 126 (1887); **4**, 235 (1889). Euler: *Ibid.*, **36**, 419 (1901).

is, the accelerating salt effect of 0.5 mole of acid is $\frac{400-275}{275}$ or 46 per cent. As the degree of ionization of 0.5 normal hydrochloric acid is 84.3 per cent, the acceleration per gram equivalent of *ionized* acid is 109 per cent. It is a most striking fact that for the same excess of acid in the case of ethyl imidobenzoate, whose velocity constant is only half as great as that of the methyl ester, McCracken[1] found an accelerating effect of 107 per cent, and for ethyl metanitroimidobenzoate, the velocity constant of which is five times greater than the methyl ester constant, the observed accelerating effect was 110 per cent per gram equivalent of ionized acid. This remarkable agreement, thus showing these values to be independent of the velocity constants themselves, seems to confirm the view of this reaction adopted here[2] and justifies the following calculation of what the velocity constant should be[3] in each experiment given in Table XIX. We have:

$$K_{calc} = 262 \times \alpha_{salt} \times (1 + m_{salt} \times \alpha_{salt} + 1.09\, m_{acid} \times \alpha_{acid}) \quad (14).$$

In the equation, 262 represents the hypothetical velocity constant of decomposition of the methyl imidobenzoate in a solution of zero concentration, that is, completely ionized and free from any salt effect whatever, including the auto-salt effect as developed by Schlesinger.[4]

The factor α_{salt} in the above equation makes the velocity of decomposition proportionate only to the concentration of the positive ion of the imidoester salt. The expression in the brackets gives the acceleration due to the effect in the solution of water produced, first, by the ions of the salt and, secondly, by the ions of the hydrochloric acid. The acceleration produced by the salt itself, according to Schlesinger's results, as above mentioned, is just about 100 per cent per mole of ionized salt, and the effect of m_{salt} moles[5] of salt,

[1] *Vide* a later paper by McCracken in THIS JOURNAL, and Stieglitz: THIS JOURNAL, **39**, 166.

[2] Stieglitz: THIS JOURNAL, **39**, 166.

[3] Stieglitz: *Loc. cit.*

[4] *Vide* a later article in THIS JOURNAL by H. I. Schlesinger.

[5] The real concentrations, m_{salt}, are found in Table XVIII. The values m'_{salt}, in Table XX, represent the ideal concentrations of an isohydric solution.

ionized to the extent of α_{salt} per cent, would be $m_{salt} \times \alpha_{salt}$. The average acceleration per 0.5 mole acid, dissociated to the extent of 84.3 per cent (in the mixed solutions), is 46 per cent, giving 1.09 as the acceleration per mole ionized acid. The acceleration due to m_{acid} mole of acid present is therefore $1.09 \times m_{acid} \times \alpha_{acid}$.

The last column in Table XX. gives the values of the velocity constant as calculated according to equation (14) and represents what the observed constants should be in each experiment if the velocity of the reaction in the equation (2′) is really a function only of the positive ion of the imidoester and of the ionization of water—the latter being considered dependent, in turn, on the total concentration of salt and acid ions present in the mixture. A comparison of the values in the last column with the actually observed constants (k_{obs}, column 5) shows, in fact, a most satisfactory agreement.

Table XX.

1	2	3	4	5	6	7
m_{acid}.	m'_{salt}.	$100\alpha_{salt}$.	$100\alpha_{acid}$.	$43430 \times k_{obs}$.	$\frac{43430\, k_{obs}}{\alpha_{salt}}$.	$43430 \times k_{calc}$.
0.0	0.0	100.0	....	...	(262)[1]	...
0.0	0.05	85.5	....	235	275	234
0.0	0.05	....	....	234	...	234
0.05	0.106	79.8	91.6	238	296	228
0.05	0.106	....	....	235	...	228
0.10	0.170	74.8	90.0	222	301	223
0.10	0.170	....	....	228	...	223
0.15	0.238	70.6	89.2	213	302	218
0.50	0.80	48.0	84.3	190	400	187
0.50	....	....	....	193	...	187

The Effect of Temperature on the Velocity Constants.

The velocity constants of the first four esters, except *n*-propyl, investigated were also determined at 18°, and in the cases of ethyl and methyl esters the reactions were followed at 0° as well. In the following table the columns and symbols have the same significance as in Table XIV. In all cases the hydrochlorides of the esters were used alone.

[1] Hypothetical, see Schlesinger: *Loc. cit.*

Table XXI.—Ethyl Imidobenzoate.

	t.	v_t.	100 x.	$10^5 k_{salt}$.
T = 18°	0	12.31	...	...
	50	11.46	6.89	143
	190	9.52	22.66	135
V = 20	280	8.42	31.59	136
s = 1	370	7.45	39.47	136
v = 25	462	6.62	46.21	135
	580	5.55	59.91	137
	1360	1.90	84.56	137
			Mean: k_{salt} = 0.00136	
T = 0°	0	12.44	...	....
	180	12.10	2.73	15.4
V = 20	480	11.57	6.99	15.1
s = 1	1230	10.43	16.17	14.3
v = 25	2670	8.43	32.24	14.6
	4210	6.82	45.17	14.3
	5620	5.46	56.11	14.7
			Mean: k_{salt} = 0.000147	

Summarizing the results given in Tables XIV. and XXI., we have as the effect of temperature on the velocity constant:[1]

T	0°	18°	25°
$10^5 k_{salt}$	15.4	136	307
Veloc. ratio	0.0502	0.433	1

Methyl Imidobenzoate.

	t.	v_t.	100 x.	$10^5 k_{salt}$
1.	0	11.08	...	...
T = 18°	45	9.99	9.82	(230)
V = 20	105	8.60	22.38	241
s = 1	195	6.82	38.44	249
v = 25	285	5.43	50.99	250
	375	4.35	60.74	249
	495	3.28	70.40	246
			Mean: k_{salt} = 0.00247	
2.	0	11.01	0.0	....
T = 0°	90	10.68	3.00	33.8
V = 20	390	9.70	11.90	32.5
s = 1	1165	7.92	28.06	28.3
v = 25	1705	6.88	37.50	27.4
	2605	5.21	52.68	28.8
	4045	3.61	67.21	27.4
			Mean: k_{salt} = 0.000297	

[1] The theoretical discussion of this effect is reserved for a later paper.—J. Stieglitz.

The effect of temperature change on the velocity constant is shown by the summary of Tables XV. and XXI.:

T	0°	18°	25°
$10^5\,k_{salt}$	29.7	247	562
Veloc. ratio	0.0529	0.440	1

Isopropyl Imidobenzoate.

	t.	v_t.	100 x.	$10^5 k_{salt}$.
1.	0	12.27	0.0	....
$T=18°$	410	10.20	16.88	45.6
$V=20$	1320	6.86	44.10	44.1
$s=1$	1820	5.37	56.24	45.4
$v=25$	2800	3.45	71.89	45.3
	3380	2.72	77.84	44.6
	4250	1.88	84.65	44.1

Mean: $k_{salt} = 0.000448$

The values of the velocity constants from Table XVII. and XXI. are:

T	18°	25°
$10^5 k_{salt}$	44.8	103
Velocity ratio	0.435	1

The Velocity of Reaction of the Free Imidoesters in Aqueous Solutions.[1]

Attention has been called to the fact that free imidoesters alone in water solution decompose very slowly, according to

$$RC(:NH)OR \rightarrow RCN + ROH \qquad (1),^2$$

and since this change is simultaneous with the main reaction of the ionized salt (the free base formed being due to hydrolytic dissociation), it was necessary to determine the velocity constant in order to correct the observed velocity constants and thus determine the true constant of the salt.[3] The two products of decomposition of the free esters are neutral substances, so that the course of the reaction could be followed

[1] See the detailed discussion of this reaction in Stieglitz's paper: This Journal, 29, 166.

[2] A nitrile is the main product. Probably a small amount of benzamide is also formed.

[3] A few calculations in which this correction has been applied are given in the footnote on page 462. It was found to be trifling.

simply by direct titration, from time to time, of measured volumes of solution with standard acid and methyl orange, taking, of course, the precautions regarding the end tint described under the analyses of the free esters. The reaction is a monomolecular one, proceeding according to

$$\frac{dx}{dt} = k_{ester} \times (C_{ester} - x),$$

and

$$k_{ester} = \frac{1}{t_2 - t_1} \log \text{nat} \frac{C - x_1}{C - x_2}.$$

The following table shows the results obtained for the various esters at 18° and 25°. The columns and symbols have the same significance as in previous tables. Owing to the slight solubilities of these esters, dilute solutions were necessarily used:

Table XXII.—Ethyl Imidobenzoic Ester.

	t.	v_t.	100 x.	$10^5 k_{ester}$.
1.	0	3.65	...	...
$T = 18°$	1240	3.10	15.1	13.2
$V = 60$	2140	2.74	24.9	13.4
$v = 25$	3560	2.25	38.4	13.6
			Mean: k_{ester} =	0.000134
2.	0	6.19	0.	...
	350	5.63	9.10	27.1
$T = 25°$	1110	4.57	26.2	27.3
$V = 40$	1580	4.01	35.2	27.5
$v = 25$	2480	3.04	50.9	28.7
	3220	2.43	60.7	29.0
	3940	1.98	68.0	28.9
	5380	1.38	77.7	27.9
	6800	0.96	84.5	27.4
			Mean: k_{ester} =	0.0002797

Methyl Imidobenzoic Ester.

1.	0	3.23	0.	...
	1790	2.57	20.4	12.8
$T = 18°$	2720	2.25	30.3	13.3
$V = 31$	4120	1.91	40.9	12.8
$v = 10$	5560	1.56	51.7	13.4
	7000	1.34	58.5	12.6
			Mean: k_{ester} =	0.000130

Table XXII—(Continued).

	t.	v_t.	$100\,x$.	$10^5 k_{ester}$.
2.	0	12.49	0.0	...
$T = 25°$	200	11.85	5.05	25.9
$V = 20$	400	11.28	9.62	25.3
$v = 25$	1340	8.66	30.6	27.3
	2750	5.72	54.2	28.4
	4200	3.75	70.0	28.6

Mean: $k_{ester} = 0.000271$

Isopropyl Imidobenzoic Ester.

1.	0	1.513	0.0	...
$T = 18°$	2340	1.319	12.8	5.85
$V = 150$	3750	1.247	17.7	5.16
$v = 25$	5180	1.141	24.6	5.45
	6600	1.054	30.3	5.48
	8070	0.962	36.4	5.61
	13890	0.696	54.0	5.59

Mean: $k_{ester} = 0.0000552$

2.	0	2.012	0.0	...
	490	1.938	(3.66)	(7.6)
$T = 25°$	1230	1.702	15.42	13.6
$V = 125$	1790	1.600	20.5	12.8
$v = 25$	2670	1.438	28.5	9.9
	4100	1.180	41.3	13.0
	5560	0.962	52.3	13.3
	7020	0.818	59.3	12.8

Mean: $k_{ester} = 0.000126$

Methyl Metanitroimidobenzoic Ester.

1.	0	2.40	0.0	...
$T = 18°$	420	2.27	7.58	(18.70)
$V = 208$	1400	2.17	9.58	9.19
$v = 50$	2730	1.95	18.76	7.69
	4170	1.74	27.5	7.71

Mean: $k_{ester} = 0.000075$

It is evident that, in every instance, good constants are obtained for a reaction proceeding with a velocity proportionate to the total concentration of the ester.

It is with pleasure that I acknowledge the painstaking care with which Professor Stieglitz directed and followed my work, and I wish to express to him my appreciation and deep gratitude for all he has helped me to accomplish.

CHICAGO, September, 1907.

THE INFLUENCE OF RADIUM ON THE DECOMPOSITION OF HYDRIODIC ACID.

By H. Jermain M. Creighton and A. Stanley Mackenzie.[1]

The first mention of the influence of radiant energy of any kind on chemical reactions was made by William Cruickshanks,[2] who observed that hydrogen and chlorine combine under the influence of light. This particular reaction has been the source of many investigations, carried out by such men as Dalton,[3] Draper,[4] Bunsen and Roscoe, and, more recently, Mellor,[5] Bevan,[6] and Burgess and Chapman.[7] Of the numerous reactions affected by light the following are some of the more important: Influence of light on silver salts, on the action of bromine and chlorine on metallic silver, on dyed colors, on enzymes in oxygen and hydrogen, on glass, on the oxidation of iodoform, on the action of oxygen on carbon bisulphide, on the decomposition of hydrogen peroxide, on the combination of hydrogen and bromine, on the reaction between chlorine and benzene.

Other forms of radiant energy whose effects on chemical action have been investigated are ultraviolet light, Röntgen rays, and radium radiations.

Only a comparatively small amount of work has been carried out on the effect of radium on chemical reactions. Hardy and Wilcocks[8] have investigated the oxidation of iodoform when acted on by Röntgen rays and by radium, and Hardy[9] has observed the coagulation of globulin under the influence of the latter rays. Becquerel[10] found that white phosphorus is changed into the inactive red phosphorus and that mercuric chloride, in the presence of oxalic acid, is reduced to mer-

[1] In this paper an investigation already published by one of us is developed and enlarged (Creighton: P. and Trans. Nova Scotia Inst. of Sc., **12**, p. 1).

[2] Nicholson's J. [1], **5**, 202 (1801).

[3] A New System of Chem. Phil., p. 300.

[4] Phil. Mag. [3], **25**, 9 (1844); **26**, 473 (1845).

[5] J. Chem. Soc., **86**, 53 (1904).

[6] P. Camb. Phil. Soc., **2**, 264–266 (1902).

[7] J. Chem. Soc., **88**, 1399 (1906).

[8] P. Roy. Soc., **72**, 200, 480.

[9] P. Phys. Soc., May 16, 1903.

[10] Compt. rend., **133**, 709 (1901).

curous chloride by the radiations from radium. The Curies[1] have shown that the rays from radium change oxygen into ozone, and discolor glass. Berthelot[2] cites the following cases: Iodic acid is decomposed by radium rays and by light, with liberation of iodine, this change being much slower than that of iodoform; nitric acid gives off nitrous fumes when acted on by radium and by light. These reactions appear to be all that have been investigated up to the present time.

These investigations have been mainly of a qualitative nature, the quantitative side receiving very little attention. The following experiments were carried out with a view to finding out whether a quantitative examination of the change, if any, produced in hydriodic acid by the presence of radium would throw light on the part played by the rays in this decomposition. Hydriodic acid was chosen on account of its instability, and from its behavior under the influence of light it was believed that it would be affected by radium rays.

The effect of light on the decomposition of hydriodic acid has been largely investigated in the last few years. Pinnow,[3] who has done a large amount of work on this subject, used acid solutions of potassium iodide for the production of the hydriodic acid. He found that the best results were obtained when the solution of potassium iodide used had a concentration of one gram per liter. It was a solution of this strength that was used in all the following work. The hydriodic acid was set free from the iodide by a solution of sulphuric acid consisting of one part of acid (sp. gr. 1.84) to five parts of water. The proportion of acid to iodide solution was one to eight.

The amount of oxidation was determined, in the usual way, by titrating the liberated iodine with 1/1250 normal sodium thiosulphate solution.

It was found that the end point could be determined very quickly and accurately by highly illuminating the solution by means of an electric light placed behind it and reflecting

[1] Compt. rend., **129**, 823 (1899).
[2] *Ibid.*, **133**, 659 (1901).
[3] Ber. d. chem. Ges., **34**, 2528 (1901).

back the rays through the solution by placing a piece of white paper around the beaker on the opposite side.

The potassium iodide used was the chemically pure, guaranteed reagent supplied by C. F. Kahlbaum.

By carrying out the titration in the above manner the error was found to be about ± 0.08 cc. sodium thiosulphate solution.

Five milligrams of radium bromide, of activity of about 1,000,000, were employed. The radium was enclosed in a small glass tube, so that only the β- and γ-rays were used.

The starting point in the investigation was to determine whether radium exerted any influence on the oxidation of hydriodic acid. For this purpose the radium was placed over a vessel containing the acid solution of potassium iodide, of the concentration mentioned above, and its rays allowed to bombard the solution for a certain time; at the end of that time the amount of decomposition was compared with that of a similar solution which had not been acted upon by radium. The vessels used to contain the solutions were ordinary wide-mouthed reagent bottles, with a capacity of about 125 cc. The small glass tube containing the radium was held in the end of a hollow brass rod which was placed in a fixed position in a wooden block; this latter fitted into the mouth of one of the bottles. Thus, by filling the bottle to a definite mark, the distance between the radium and the surface of the liquid was always kept the same. The distance was between two and three millimeters.

These experiments were all carried out in a photographic dark room, so that there was no chance of the reaction being influenced by light. The solution which was not to be acted upon by radium was protected from the rays by a screen of lead, so placed that the solution would not be affected appreciably by the secondary rays set up in the lead.

Several experiments carried out in this way showed, at the end of twenty-four hours, that the decomposition in the solution acted upon by radium was greater than the decomposition in the other; but the excess varied in different trials from 15 per cent to 25 per cent. In order to obtain more con-

cordant results for similar experiments the temperature at which the reaction took place was kept constant for a series of measurements, and it was found that this made a decided improvement in the agreement of the results. It was still found, however, that the differences in results under similar conditions were considerably greater than those due to experimental error. In order to see whether these differences were due to small errors in the mixing of the solutions, a large quantity of solution was prepared and divided into six equal parts of 225 cc. each. These were allowed to stand for twenty hours in a dark room, without radium, at a temperature of $16° \pm 0°.5$ C. At the end of that time the amount of decomposition, as measured by the number of cc. of titrating solution required, was found to be, for the several portions, 5.38, 5.23, 5.41, 5.34, 5.07, 5.33, respectively. The lack of equality of these numbers shows that the irregularity is not to be accounted for in this way.

The influence of the impurities in the ordinary distilled water used in making up the solutions was next investigated, and it was found that when the water had a conductivity, expressed in Kohlrausch's unit,[1] (ohm^{-1} $cm.^{-1}$), of 2.0×10^{-6}, or less, at 18° C., the agreement between the amounts of decomposition of several similar solutions was within the limit of experimental error.

The water used in the following experiments was prepared according to the method of Jones and Mackay.[2] The ordinary distilled water was doubly distilled. The steam from the first flask, which contained the water mixed with an alkaline solution of potassium permanganate, was bubbled through an acid solution of potassium bichromate in a second flask. Into the neck of the latter was thrust a block-tin condenser, which was held there by means of a cork made of a mixture of plaster of Paris and asbestos. The water thus obtained had a mean conductivity of 1.6×10^{-6} at 18° C. It was kept in bottles which had been used several years for that purpose.

It was found that the purity of the water, as determined

[1] Kohlrausch und Holborn: "Leitvermögen der Elektrolyte," 1898, p. 1.
[2] Z. physik. Chem., **22**, 237 (1897).

by its conductivity, played an important part in the rate of decomposition of the solution. The table below shows the results obtained when using water of two different grades of purity in the preparation of the solutions.

In this table, and those that follow, the numbers given denote the amount of 1/1250 normal sodium thiosulphate solution required to titrate the free iodine content in the hydriodic acid solution at the times specified after the instant of mixing. The mixing was done in the dark room. In all cases the amount of hydriodic acid solution experimented upon was 50 cc.

The numbers in the following table are for the case where the mixture was left to stand in the dark room, and was not subjected to the action of radium or any other external action. The temperature was 15° ± 0°.5 C.

Table I.

Time in hours.	No. of cc. of N/1250 $Na_2S_2O_3$ solution required in titration when hydriodic acid solutions were made up with water of conductivity 4.98×10^{-6}.	conductivity 2.16×10^{-6}.
7	0.73	0.90
11	0.97	1.04
15	1.38	1.40
20	1.68	1.63
25	2.05	....
30	2.45	1.79
35	2.80	....
40	2.86	1.95
50	3.20	....
70	4.05	....
95	4.37	3.08
120	4.25	3.35
170	3.75	3.24
200	3.24	3.24
300	3.45	3.22
380	1.58	3.23
450	....	3.21
550	....	3.25
650	0.89	3.20
1100	....	3.24

From an examination of this table it will be seen that there is a striking difference between the behavior of solutions

made up with ordinary distilled water and of those made up with water which had been more carefully purified. For the less pure water the content of free iodine rose to a maximum in about four days, and then gradually fell off again; but with the purer water the iodine content increased with the time for the first five days, and then remained constant for the next six weeks during which it was under observation. Similar hydriodic acid solutions made up with the less pure water were subjected to sunlight, and in that case also the amount of iodine increased at first, reached a maximum after some days, and finally disappeared entirely. Hence the effect of impurity in the water is of the same nature whether the solution be left in the dark or acted on by sunlight. It will be seen later that in certain circumstances radium has the same effect on solutions made up with the purer water.

It would seem that the effect of the small amount of impurity in the water is to cause the formation, by some sort of catalytic action, of a third iodine product in addition to the hydriodic acid and free iodine which alone we might at first sight expect. In the case of solutions made up with the purer water, where the iodine content tends towards a constant asymptotic value, as given in the third column of the above table, the simplest explanation is that the third product is not being formed, and that we have there the ordinary equilibrium between the hydriodic acid, the hydrogen, and the iodine. If the third product is still being formed, two suggestions present themselves to account for the continued constancy of the amount of free iodine present: (1) that the rate of formation of the third product is very small, but that in time the numbers in the last column of the table would begin to decrease also; (2) that the whole system reaches a state of equilibrium, and the iodine content will be constant however long the time. The former suggestion is the more probable one, since it is likely that even by the more careful distillation of the water we have not entirely got rid of the cause of the trouble but only reduced it in amount.

This, however, is not the only effect of the impurity in the water; it also accelerates the rate of accumulation of iodine.

This is evident from the fact that the maximum value reached in the case of the less pure water is greater than the asymptotic value approached in the case of the purer sample. As it was found that the rate of production of free iodine was much affected by the temperature, it was felt that an answer to the question of whether radium radiations had a specific action of their own on hydriodic acid or only changed in degree the action going on in their absence was to be looked for from a study of the action at different temperatures both in the presence and in the absence of radium. Further efforts at an explanation of the action of external agencies, such as impurity, light, Becquerel rays, etc., will therefore be deferred until the experiments on the effect of temperature on solutions with and without radium have been detailed.

The following table contains the results obtained with water of a high degree of purity, at a temperature of 24° C., both with and without radium. A new sample of 50 cc. of hydriodic acid solution was taken for each period of time shown.

Table II.

No. of cc. of N/1250 $Na_2S_2O_3$ solution required in titration when the decomposition of hydriodic acid solution takes place in the dark in the presence of

	no radium		radium	
Time in hours.	observed.	calculated from $y = a(1-e^{-bt})$; $a = 1.54$, $b = 0.175$.	observed.	calculated from $y = a(1-e^{-bt})$; $a = 2.10$, $b = 0.175$.
2	0.45	0.45	0.58	0.62
3	0.65	0.63	0.85	0.86
5	0.92	0.90	1.25	1.23
7	1.10	1.09	1.51	1.48
10	1.23	1.27	1.73	1.73
12	1.27	1.35	1.77	1.85
16	1.38	1.45	1.94	1.98
21	1.52	1.50	2.10	2.05
38	1.56	1.54	2.09	2.10

In the third and fifth columns of the table are added numbers calculated from the equation

$$y = a(1 - e^{-bt}) \qquad (1),$$

with the values of a and b there given, to show how well the observations are represented by curves of this type. These

calculated curves are plotted as N(24°) and R(24°) in Fig. I., the amounts of sodium thiosulphate solution being represented as ordinates, and the times as abscissas. The observed values are marked, and lie remarkably well on the curves.

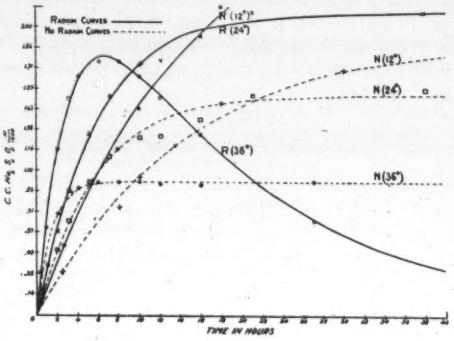


Fig. I.

The similarity of the two curves seems to show that with pure water, at this temperature, the action of the radium is of the same nature as that which goes on without it in the dark, but is greater.

The reaction was next observed at 12° C., and a few readings made to determine the behavior at that temperature. The results are given in the following table:

Table III.

No. of cc. of N/1250 $Na_2S_2O_3$ solution required in titration when the decomposition of hydriodic acid solution takes place in the dark in the presence of

	no radium		radium	
Time in hours.	observed.	calculated from $y = a(1-e^{-bt})$; $a = 1.92$, $b = 0.07$.	observed.	calculated from $y = a(1-e^{-bt})$; $a = 2.50$, $b = 0.07$.
2.5	0.30	0.31	0.49	0.46
8	0.75	0.83	1.15	1.25
10	0.95	0.96	1.43	1.46
18	1.47	1.37	2.15	2.08
30	1.69	1.69	2.55	2.55

The curves for this case are those marked N(12°) and R(12°) in Fig. I. The only difference between the behavior at this temperature and that at 24° is that at the former the decomposition of the solution is much slower, and the equilibrium values are consequently greater and longer in being reached. The effect of the radium is again, apparently, only to increase the action in degree but not to change it in type.

The next experiments were made at 36°, and the results are shown in Table IV.:

Table IV.

No. of cc. of N/1250 $Na_2S_2O_3$ solution required in titration when the decomposition of hydriodic acid solution takes place in the dark in the presence of

	no radium		radium	
Time in hours.	observed.	calculated from $y = a(1-e^{-bt})$; $a = 0.92$, $b = 0.70$.	observed.	calculated from $y = a(e^{-bt}-e^{-ct})$; $a = 3.3$, $b = 0.06$, $c = 0.31$.
0.5	0.18	0.27	0.30	0.38
1	0.35	0.46	0.60	0.69
2	0.70	0.69	1.15	1.15
3	0.85	0.81	1.50	1.46
4	0.88	0.87	1.65	1.64
6	0.93	0.91	1.75	1.79
8	0.92	0.92	1.75	1.75
10	0.93	0.92	1.65	1.64
12	0.91	0.92	1.50	1.52
16	0.90	0.92	1.25	1.24
27	0.93	0.92	0.65	0.65

The curves for this case are marked N(36°) and R(36°) in Fig. I. It will be seen that the curve for no radium, N(36°), is still of the same logarithmic form as the curves for no radium and radium at both 12° and 24°. A comparison of the no radium curves for 12°, 24°, and 36° shows that as the temperature increases the times taken to reach the equilibrium value decrease, being approximately 60, 23 and 6 hours, respectively; and the equilibrium values correspondingly decrease, being 1.92, 1.54, and 0.92, respectively. This denotes an increased rate of formation of free iodine as the temperature is increased. The same thing is true of the radium curves for 12° and 24°. The radium curve for 36°, R(36°), however, is of an entirely different form from these five; it rises steeply toward a maximum, and then steadily falls off

again. It has exactly the same form as the curve for impure water with no radium, which we considered earlier. It is most probable that this is more than a coincidence, and it is reasonable to suppose that what the impurity does at the lower temperature the radium also does at this higher temperature.

The form of the curve R(36°) suggests an equation of the type

$$y = a(e^{-bt} - e^{-ct}) \qquad (2).$$

It is well known that for this equation the latter part of the downward slope of the curve is practically determined by the smaller of the two quantities b and c. Accordingly, from the observed values of y at 12, 16, and 27 hours, b was found to be 0.06 and a to be 3.3. The value of c can be found from the fact that at the maximum, calling the time at this instant T hours, we have the relation

$$be^{-bT} = ce^{-cT}.$$

Putting for T the value 6.6, found from the curve, and for b its value 0.06, we find c to be 0.31. The numbers calculated from equation (2) with these values of the constants are given in the last column of Table IV., and the agreement with the observed values falls well within the limit of error.

It is now necessary to frame an hypothesis of what is going on which will be consistent with the known properties of the chemical substances used, and with the behavior observed experimentally.

The reaction between H_2SO_4 and KI is presumably a bimolecular, reversible one, and since the solution, as mixed, contains 65 equivalents of acid to 1 of iodide, we would be inclined to suppose that the equilibrium value of HI is nearly equal to the amount of KI used, and is reached in a comparatively short time. If we knew the values of the direct and reverse rates of the reversible reaction this could be quickly tested, but these constants we have been unable to find. Differential equations were formed after the manner of those given below and solved on the supposition that the HI is formed slowly from the KI, but this supposition failed entirely to fit in with all the experimental results. Accord-

ingly, in what follows the HI, as a first approximation, is assumed to be formed instantaneously and to the maximum amount. This latter amount is 336, when expressed in cc. of N/1250 sodium thiosulphate solution, the unit in which all our observed numbers are expressed. This assumption does not seem to be in accord with the observations of Pinnow,[1] who found that the amounts of thiosulphate required in titration were proportional to the number of equivalents of acid used with one equivalent of iodide, but it is to be remembered that he was measuring the content of free iodine, not of HI. His results could be made to accord with our assumption if we suppose that the sulphuric acid stimulated the change of HI into free iodine.

Perhaps the most obvious supposition to make in order to account for the decrease of free iodine after 7 hours, when the reaction takes place at 36° under the influence of radium, is that the iodine is being transformed into a third product. We can easily find an equation for the amount of free iodine at any time, in this case, if we consider that the reactions which take place are monomolecular. Call n the total initial amount of HI, and x the amount at any time t. Call y the amount of free iodine at that time. Let k_1 and k_2 be the direct and the reverse velocity constants in the reversible reaction $HI \rightleftarrows H+I$, and λ the similar quantity in the conversion of the iodine into a third product. We have to solve the equations

$$\left.\begin{aligned} \frac{dx}{dt} &= k_2 y - k_1 x; \qquad x = n, \text{ if } t = 0; \\ \frac{dy}{dt} &= k_1 x - (k_2 + \lambda) y; \quad y = 0, \text{ if } t = 0. \end{aligned}\right\}$$

The value of y at any time is

$$y = \frac{nk_1}{2\beta}\left[e^{(\alpha+\beta)t} - e^{(\alpha-\beta)t}\right] \qquad (3),$$

$$\left.\begin{aligned} \text{where } \alpha &= -\frac{1}{2}\left[k_1 + k_2 + \lambda\right], \\ \beta &= \frac{1}{2}\sqrt{(k_1 + k_2 + \lambda)^2 - 4k_1\lambda} \end{aligned}\right\} \qquad (4).$$

[1] *Loc. cit.*

When $4k_1\lambda$ is very small as compared with $(k_1 + k_2 + \lambda)^2$, equation (3) takes the form of equation (1); otherwise it has the form of equation (2). If we make $\lambda = 0$, or $k_2 = 0$, and $4k_1\lambda$ small, equation (3) becomes

$$y = \frac{nk_1}{k_1 + k_2}\left[1 - e^{-(k_1 + k_2)t}\right], \text{ or } y = \frac{nk_1}{k_1 + \lambda}\left[1 - e^{-(k_1 + \lambda)t}\right],$$

and values of k_1, and k_2 or λ, as the case may be, can be found consistent with the observations in all cases observed, except for 36° with radium. When for this latter case, we give $4k_1\lambda$ the value necessary to make $\alpha + \beta = -0.06$, and $\alpha - \beta = -0.31$, as is required by the last column of Table IV., it is soon seen from the form of equations (3) and (4) that the minimum value of k_1 possible is far too large to give numbers for y in keeping with observed values. Accordingly this explanation of what is going on had to be abandoned.

Another explanation was found more amenable, that the third product is formed, not from the free iodine, but from the hydriodic acid. Call λ, now, the rate of formation of this product. With the same notation, otherwise, as before, our equations take the form

$$\left.\begin{aligned} \frac{dx}{dt} &= k_2 y - (k_1 + \lambda)x\,; \quad x = n, \text{ if } t = 0; \\ \frac{dy}{dt} &= k_1 x - k_2 y\,; \qquad\qquad y = 0, \text{ if } t = 0. \end{aligned}\right\}$$

The value of y at any time now is

$$y = \frac{nk_1}{2\beta}\left[e^{(\alpha + \beta)t} - e^{(\alpha - \beta)t}\right] \qquad (5),$$

$$\left.\begin{aligned} \text{where } \alpha &= -\frac{1}{2}(k_1 + k_2 + \lambda), \\ \beta &= \frac{1}{2}\sqrt{(k_1 + k_2 + \lambda)^2 - 4k_2\lambda} \end{aligned}\right\} \qquad (6).$$

These equations are of the same form as equations (3) and (4), except that $4k_2\lambda$ enters, instead of $4k_1\lambda$, as the quantity upon which the form of the curve in y and t turns. As before, we get equations of the type of equation (1) when $4k_2\lambda$ is exceedingly small as compared with $(k_1 + k_2 + \lambda)^2$, and

of the type of equation (2) when this is not so. Moreover, the values of y, being directly proportional to k_1, can now be made to agree with those observed for radium at 36° as well as for the other five cases, because now the determining quantity $4k_2\lambda$ does not contain k_1. It will be noticed that the quantities k_2 and λ are interchangeable in equations (5) and (6), so that it will be impossible to distinguish between them, when the equation is applied to our observations, without some other evidence. The following table contains the values of the constants which, when put in equation (5), will be in agreement with the experimental observations.

Table V.

	12°		24°		36°	
	No radium.	Radium.	No radium.	Radium.	No radium.	Radium.
k_1	0.00040	0.00061	0.00081	0.00110	0.00192	0.00249
k_2 (or λ)	0.07	0.07	0.175	0.175	0.70	0.31
λ (or k_2)	small	small	small	small	small	0.06
$k_1+k_2+\lambda$	0.0704	0.0706	0.1758	0.1761	0.7019	0.3725
a	1.92	2.90	1.54	2.10	0.92	3.30

Some idea of the size of the smaller of the two quantities k_2 and λ, in the neighborhood of 12°, may be had from the fact that we saw that at 15° there was no decrease of the amount of iodine after the lapse of 1100 hours when the radium was not present. Taking the case of no radium at 12°, and assuming that $k_2\lambda$ has a value, even if small, equation (5) becomes

$$y = \frac{nk_1}{2\beta}\left[e^{-\frac{k_2\lambda}{k_1+k_2+\lambda}t} - e^{-(k_1+k_2+\lambda)t}\right],$$

approximately. If $\frac{k_2\lambda}{k_1+k_2+\lambda}$ 1100 is as great as 0.01, since one of the factors, k_2 or λ, is about equal to $k_1+k_2+\lambda$, the other is of the order of magnitude of 0.00001, at most, and probably much smaller. Further work is now in progress which, it is hoped, will make it possible to determine whether k_2 or λ is the small quantity.

The chief justification for considering the reactions involved as monomolecular is that this supposition gives an

explanation consistent with the observed behavior. The recombination of the hydrogen and iodine is at first sight bimolecular, but if the solution contains a large number of free hydrogen ions the action would appear monomolecular. Similarly, if the sulphuric acid takes part in the formation of the third product, that reaction might well appear monomolecular, as the concentration of the acid would not vary materially. It may also be worthy of notice that if the equilibrium value of HI formed by the action of the acid on the iodide were less than the possible maximum, 336, but were reached in a relatively short time, our equation would hold for a large number of hours to a fair degree of approximation. This would make it necessary to put for n in equation (5) a number smaller than 336, and would make all our values of k_1 proportionately greater.

The following general conclusions can be drawn from the numbers in Table V.:

1. The rate of transference, k_1, of HI into H and I, both in the presence and in the absence of radium, increases with increase of temperature.

2. At any temperature, the rate of transference, k_1, of HI into H and I is increased by the presence of radium; the effect of the radium is relatively smaller, the higher the temperature.

3. The constant of the larger of the two retarding factors which keeps down the amount of iodine present at any time (whether it is k_2 or λ, we do not know) increases with increase of temperature, and to a greater extent than does the accelerating constant k_1.

4. The constant of the larger of the two retarding factors is very slightly affected by the presence of radium at the lower temperatures.

5. Whereas at the lower temperatures the action of the radium increases the rates of the accelerating and retarding actions, at 36° it introduces an entirely new (or magnifies a previously existing infinitesimal) retarding reaction, at the same time reducing the retarding action already existing.

Effect of Temperature.

In order to show the effect of temperature alone, both when the solution is under the influence of radium and without it, the reaction was allowed to proceed for ten hours at various temperatures. The results were as follows:

Table VI.

Temperature C.	No. of cc. of N/1250 $Na_2S_2O_3$ solution required in titration when the decomposition of hydriodic acid solution takes place in the dark in the presence of		Difference.
	no radium.	radium.	
0	0.20	0.78	0.58
4	0.45	1.02	0.57
8	0.68	1.21	0.53
12	0.95	1.43	0.48
16	1.20	1.73	0.53
20	1.25	1.75	0.50
24	1.23	1.73	0.50
36	0.93	1.65	0.72
Mean of all differences except that for 36°,			0.53

These observations are plotted in Fig. II. It will be noticed that these temperature curves run parallel from 0° to about 25°, but that thereafter the no radium curve begins to drop faster than the radium curve. This change from parallelism is evidently coincident with the appearance of the change of

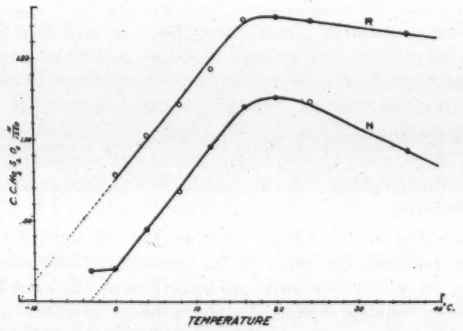


Fig. II.

type of the radium curve which we saw was so noticeable at 36°. It seems from the measurements at hand that the temperature curves would exhibit this same parallelism up to 25° for any number of hours less than 10 during which the reaction is observed; but as the time of observation is taken longer the amount by which the radium curve is higher than the no radium curve falls off with the temperature, and they are not parallel at any part of their course. It is worthy of notice that if we had based our conclusions as to the behavior of radium on a study of the temperature curves for any period of time up to 10 hours at ordinary temperatures, we should have been tempted to say that the action of radium was a purely additive one and that the radium had its own separate action apart from that which was going on in its absence, whereas consideration of the values of the constants in Table V. leads us to believe that the action of radium is intensive, and not additive, at least for ordinary temperatures.

It is further worthy of notice that for the range 0° to 16° the curves are straight lines. If these lines were produced they would cut the axis of temperatures at —12° for radium, and —3.°2 for no radium; that is, if these lines remain straight, the decomposition at the end of 10 hours would be zero if the solution is kept at —12° in the presence of radium, but it would be zero at —3°.2 with no radium. It was out of the question to keep the solution at —12° without freezing, but it was not difficult to keep it at about —3° for a time. This was done by placing the solution in a bath of very dilute alcohol surrounded by a freezing mixture. At the end of 10 hours it was found that the solution without radium had decomposed to the extent of 0.19 cc. of thiosulphate solution. Hence the curves at about 0° must cease to be straight lines and begin to run asymptotically toward the axis of temperature.

Action of γ-Rays Alone.

Hardy and Wilcocks[1] have shown that the γ-rays from radium accelerate slightly the decomposition of iodoform, but that the acceleration is small as compared with that due to

[1] *Loc. cit.*

the β-rays. In order to determine whether γ-rays behave in a similar way upon the hydriodic acid reaction under consideration, the rays from radium were made to pass through 6 mm. of lead before entering the solution. This thickness of lead is sufficient to absorb all but the very fastest β-rays, and does not absorb appreciably the γ-rays. The reaction was first allowed to go on for ten hours at 24° C., when the amount of free iodine was found to be equivalent to 2.10 cc. of thiosulphate solution. For the sake of comparison the results for ten hours at this temperature are here grouped:

No radium for 10 hours at 24°, 1.23 cc. N/1250 $Na_2S_2O_3$ solution.

$\beta + \gamma$-Rays for 10 hours at 24°, 1.73 cc. N/1250 $Na_2S_2O_3$ solution.

γ-Rays for 10 hours at 24°, 2.10 cc. N/1250 $Na_2S_2O_3$ solution.

We thus see that in this case there is much more free iodine when the γ-rays alone act than when the β-rays act along with the γ-rays. The chief difference between the conditions of the last experiment and the other two is that the radium was about 5 mm. further away from the solution when the γ-rays alone were used. The effect of this would have been to reduce the amount of decomposition, and not to increase it, as actually happened. The only other difference in conditions is the introduction of secondary radiations from the lead used to cut off the β-rays, and we would not expect their effect to more than make up for the β-rays cut out.

This increase in the amount of free iodine observed with the γ-rays alone does not seem, therefore, in accord with the results of Hardy and Wilcocks, nor does it seem at first sight to be reasonable or possible. Further consideration will show, however, that such a result can be quite in keeping with the views before expressed of what is going on. The amount of free iodine at any time is determined by the accelerating influence represented by k_1, and by the two retarding influences represented by k_2 and λ. If one, or both, of these retarding influences is not brought so much into play by the γ-rays alone as by the β- and γ-rays together, the amount

of free iodine would be increased, even if the value of k_1 were as great for the γ-rays alone as for the β- and γ-rays together.

The only other observation made with γ-rays alone was for three hours at 24°. Comparing it with the corresponding ones, we have:

No radium for 3 hours at 24°, 0.65 cc. N/1250 $Na_2S_2O_3$ solution.

$\beta + \gamma$-Rays for 3 hours at 24°, 0.85 cc. N/1250 $Na_2S_2O_3$ solution.

γ-Rays for 3 hours at 24°, 0.72 cc. N/1250 $Na_2S_2O_3$ solution.

In this case the γ-ray effect is intermediate between the other two, but the numbers are too nearly alike to base a conclusion upon them. Further experiments are to be made to decide whether the proposed explanation is the true one.

Influence of Sunlight and Radium in the Absence of Oxygen.

If a hydriodic acid solution, such as was used in the preceding experiments, was entirely freed from air and placed in a tube from which all the air had been removed, it was found that this tube could be placed in the sunlight for any length of time without the solution showing any decomposition. In order to remove all occluded air the tube, before being sealed off, was kept in the dark under a good vacuum for 24 hours, for otherwise it is found that extremely minute quantities of dissolved air will decompose slightly the hydriodic acid.

The same experiment was then tried with radium, instead of sunlight. In order to keep the solution in a vacuum for two or three days, without sealing the radium up in a tube with the solution, the vessel containing the solution with the radium above it, as before described, was placed on a plate under a bell jar connected by a glass tube with a "Geryk" pump. The joint between the jar and plate was sealed with the preparation made by heating together equal parts of India rubber, paraffin, and vaseline. When the vacuum was secured, the bell jar was sealed off from the pump. A delicate manometer connected with the jar showed no change

in vacuum at the end of several days. It was found that the radium also produced no effect.

The experiment was tried at room temperature only.

Summary.

1. When prepared with very pure water a hydriodic acid solution decomposes in the dark, reaching an equilibrium value (experiments made up to 36° C.).

2. Ordinary distilled water contains impurities producing some catalytic action which accelerates the decomposition of hydriodic acid solution in the dark, at the same time introducing another reaction which causes the amount of free iodine to reach a maximum value and then fall off indefinitely (experiment made at 15° C. only).

3. At any temperature up to 24° C. more iodine is liberated in any given time from a solution of hydriodic acid in the dark under the influence of radium than from one which is not so influenced.

4. When the experiment is tried at 36° C., this last statement is only true up to 22 hours, for, whereas the amount of free iodine with no radium reaches an equilibrium value, with radium it reaches a maximum and then falls off indefinitely.

5. At 36° C. radium seems to cause the formation of the same third product which impurity in the water produces at low temperature.

6. In general, rise in temperature tends to increase the amount of free iodine at any time, whether radium is used or not.

7. The amount of free iodine at any time depends on three quantities: an accelerating factor depending upon the rate at which HI breaks up into H and I; and two retarding factors, the one depending upon the rate at which H and I recombine and the other upon the rate at which HI enters into another reaction. One of these two retarding factors is not appreciable for temperatures as low as 24° C. (see conclusions after Table V.).

8. The γ-rays alone cause more iodine to be set free than

do the β- and γ-rays together; this is probably due to the β-rays increasing the retarding factors more than do the γ-rays (experiment made at 24° C. only).

9. Neither sunlight nor radium causes decomposition of hydriodic acid solution in the absence of oxygen (experiments made at room temperatures only).

This investigation was carried out in the chemical laboratory of Dalhousie University, and in conclusion we wish to thank Professor E. Mackay for his suggestions and valuable criticisms during the progress of the work.

DALHOUSIE UNIVERSITY,
HALIFAX, N. S.,
October 15, 1907.

[Contributions from the Chemical Laboratory of Harvard College.]

SOME DERIVATIVES OF TETRACHLORORTHOBENZOQUINONE.

BY C. LORING JACKSON AND P. W. CARLETON.

This paper contains an account of the continuation of the work on tetrachlororthobenzoquinone begun by Dr. MacLaurin and one of us.[1]

If equal weights of tetrachlororthoquinone and tetrachlorpyrocatechin, dissolved in the smallest possible amounts of hot chloroform, are mixed and the mixture cooled as quickly as possible, black needles of octochlororthoquinhydrone are deposited; but if, instead, the mixed solutions are kept warm for some time, the product is the yellow heptachlororthoquinopyrocatechin hemiether, the formation of which is accompanied by evolution of hydrochloric acid.

The orthoquinhydrone, dried *in vacuo*, gave, on analysis, percentages of chlorine corresponding to the formula

$$C_6Cl_4O_2C_6Cl_4O_2H_2.\tfrac{1}{2}H_2O.$$

As it is decomposed by heat we could not determine the amount of water directly, but think we are right in assigning this formula to it for the following reasons. Since five analyses of different specimens gave concordant results, the low per-

[1] THIS JOURNAL, **37**, 7 (1907); **38**, 120 (1907).

centage of chlorine must be due to a constant constituent rather than to a mixture with an impurity. Further, the only probable impurity which could lower the percentage of chlorine is the heptachlor hemiether, and our quinhydrone must have contained about 25 per cent of this substance to reduce the percentage of chlorine to that found, but it would be impossible that such a quantity of a yellow impurity could be overlooked among the well formed, shining, black needles of the quinhydrone. The quinhydrone is also formed when benzene is used as the solvent instead of chloroform, and we have observed no tendency to the formation of the hemiether in benzene solution. We can therefore reject an admixture of the hemiether as an explanation of the low percentages of chlorine. The only other theory we can find is that they must be caused by the addition of some substance to the molecule and as this substance is added both in chloroform and benzene solution, it can be nothing but water. This conclusion is confirmed by the fact that the crystals effloresce on drying; and, further, Russe and one of us[1] found that the octobromorthoquinhydrone crystallizes with one molecule of water, so that there is good reason to expect that the chlor compound would behave in the same way. In fact, we think it probable that our compound also crystallizes with one molecule of water, half of which is given off on drying *in vacuo*, thus explaining the effloresced appearance of the dried compound, but unfortunately, this idea occurred to us so late that we could not test it by experiment. It is certainly surprising that these compounds should take up water from ordinary chloroform or benzene, but this striking attraction for water, enabling the substance to abstract it even from liquids containing only traces of it, has been observed more than once with derivatives of the orthoquinones.[2] The quinhydrone turns yellow when heated to 70°, probably from the formation of the hemiether, and seems to be dissociated into its components, when dissolved, as would be expected from what is known of paraquinhydrones.[3]

[1] This Journal, **35**, 174 (1906).
[2] *Ibid.*, **31**, 109 (1904).
[3] Torrey and Hardenbergh: This Journal, **33**, 167 (1905).

The heptachlororthoquinopyrocatechin hemiether,

$$C_6Cl_4OHOC_6Cl_3O_2,$$

crystallizes, with some difficulty, in scales, melting with decomposition at 214°. Its most striking property is its strong tendency to lose a molecule of hydrochloric acid and pass into the red ether $C_6Cl_4O_2C_6Cl_2O_2$. This change takes place slowly and partially, even at ordinary temperatures if it is exposed to air and light, more rapidly on heating, and is also brought about by the action of alcohol. Neither of these reactions, however, ran quantitatively, as a specimen heated to 110°–140°, although it lost quickly about half of the calculated amount of hydrochloric acid, retained the second half so firmly that even after 8 weeks' heating we did not succeed in bringing the loss much above 75 per cent of the theory. With alcohol the loss was a little less than 67 per cent, and in this case impurities were detected in the red ether, pointing to the occurrence of secondary reactions. This result is certainly unexpected, as the formula of the hemiether seems to require a quantitative transformation.

MacLaurin and one of us,[1] by the action of benzaldehyde or acetone on tetrachlororthoquinone, obtained a yellow product, which was supposed to be this heptachlor hemiether, but seemed so unstable that it could not be purified or studied. It has happened before in work with the orthoquinones that an impure product was converted into the red ether $C_6Cl_4O_2C_6Cl_2O_2$ by conditions which did not affect the pure substance.

We have found easy methods for the preparation of two of the substances discovered by MacLaurin and one of us. Thus the hexachlororthoquinomethylmonohemiacetalpyrocatechin ether,[2] $C_6Cl_4O_2C_6Cl_2O(OCH_3OH)$, melting at 198°, can be made by boiling the ether $C_6Cl_4O_2C_6Cl_2O_2$ with methyl alcohol; and the hexachlororthoquinomethylhemiacetalpyrocatechin ether,[3] $C_6Cl_4O_2C_6Cl_2(OCH_3OH)_2$, melting at 218°, can be made by the action of sodic methylate on the same ether.

[1] This Journal, **37**, 10 (1907).
[2] *Ibid.*, **38**, 150 (1907).
[3] *Ibid.*, **38**, 154 (1907).

The monohemiacetal melting at 198° was converted into a methylacetacetal, $C_6Cl_4O_2C_6Cl_2O(OCH_3OC_2H_3O)$, melting at 220°, by treatment with acetic anhydride. This substance was prepared by MacLaurin and one of us,[1] who found the melting point 215°, but supposed that it had the composition of a diacetoxypyrocatechin ether, $C_6Cl_4O_2C_6Cl_2(OC_2H_3O)_2$, since the only chlorine determination made agreed with this (calculated Cl = 42.01. Found, Cl = 42.49. $C_6Cl_4O_2C_6Cl_2O(OCH_3OC_2H_3O)$, Cl = 43.03), and its formation seemed to have been preceded by the conversion of the hemiacetal into the red orthoquinopyrocatechin ether. The work described in this paper showed that the red impurity appearing during the action of acetic anhydride is not the ether, and is formed in such small amount as not to influence the nature of the product; and our analyses prove that the main product is the acet compound, $C_6Cl_4O_2C_6Cl_2O(OCH_3OC_2H_3O)$, thus furnishing a welcome confirmation of the monomethylhemiacetal formula, $C_6Cl_4O_2C_6Cl_2O(OCH_3OH)$, ascribed to the mother substance on grounds which were not absolutely convincing.

A set of preliminary experiments has made it probable that acetophenone enters into a compound with tetrachlororthoquinone; and another set, in which tetrachlorpyrocatechin was oxidized with fuming nitric acid containing a little hydrochloric acid, gave a yellow product, which may be identical with the substance isolated by MacLaurin and one of us[2] from the mother liquors of the tetrachlorpyrocatechin preparation, after they had stood seven months with an excess of chlorine. It is hoped that both these substances will be studied in this laboratory in the coming year.

EXPERIMENTAL.

Preparation of Tetrachlororthobenzoquinone.—The method adopted for making the tetrachlorpyrocatechin was that described by MacLaurin and one of us.[3] In the hope of avoiding a large use of glacial acetic acid, some experiments were

[1] THIS JOURNAL, **38**, 153 (1907).
[2] *Ibid.*, **37**, 19 (1907).
[3] *Ibid.* **37**, 11 (1907).

tried on purifying it with alcohol but, although good results were obtained, we found it more satisfactory to return to the crystallization from glacial acetic acid. Successive portions were recrystallized from the same quantity so as to reduce the amount washed in the mother liquors and the use of the expensive solvent. The yield in this case was quantitative after the first crystallization, and the product remained of satisfactory color and melting point during a large number of operations. After the acetic acid became so loaded with impurities as to give colored crystals, it was distilled, and in this way the greater part of it recovered. The glacial acetic acid in which the tetrachlorpyrocatechin was made was also recovered by distillation. In either case the residue was a black, tarry mass too impure to make it worth while to try to extract any tetrachlorpyrocatechin from it.

In converting the tetrachlorpyrocatechin into the corresponding quinone, a considerable saving of glacial acetic acid was effected by adopting the method found by Flint[1] to work well with the tetrabromorthoquinone. The tetrachlorpyrocatechin was dissolved in alcohol, using 1 or 1.5 parts of solvent to 1 part of the solid, and to this solution was added fuming nitric acid diluted with 6 parts of glacial acetic acid, the process being identical with that of MacLaurin in other respects. This method worked well if the amount of substance was small and the temperature was kept low. The yield was from 75–80 per cent of the theory (MacLaurin obtained 81.5 per cent), and, although the melting point of the product was not above 127° (MacLaurin's average was 133°), it was pure enough for our purposes.

Octochlororthobenzoquinhydrone, $C_6Cl_4O_2C_6Cl_4O_2H_2.\frac{1}{2}H_2O$.—This substance was made by dissolving equal weights of tetrachlorpyrocatechin and tetrachlororthoquinone separately in small quantities of hot chloroform, mixing the two solutions and cooling rapidly, when a large quantity of long, black needles separated. The crystals were filtered out, dried on filter paper and then *in vacuo* over sulphuric acid and soft paraffine, when they lost their brilliant lustre, turning to a dull purple.

[1] This Journal, **39**, 83 (1908).

In preparing this compound the operations must be carried through as rapidly as possible since, if the substance was allowed to stand with the chloroform, especially if it was hot, the yellow heptachlororthoquinopyrocatechin hemiether (described later) was formed. If benzene was used as the solvent, the quinhydrone was also obtained (Analysis IV.), but in this case there was a tendency for part of the constituents to remain uncombined. As the substance could not be dissolved without decomposition, it was analyzed with no attempt at purification.

I. 0.2106 gram substance gave 0.4828 gram AgCl.
II. 0.1688 gram substance gave 0.3878 gram AgCl.
III. 0.1548 gram substance gave 0.3530 gram AgCl.
IV. 0.1818 gram substance gave 0.4136 gram AgCl.
V. 0.1694 gram substance gave 0.3889 gram AgCl.

	Calculated for $C_6Cl_4O_2C_6Cl_4O_2H_2.\frac{1}{2}H_2O$.	Found. I.	II.	III.	IV.	V.
Cl	56.46	56.68	56.79	56.39	56.26	56.74

These analyses agree with each other and the theory as closely as was to be expected with a substance that could not be purified. The reasons for adopting the formula with $\frac{1}{2}H_2O$ have been given in the introduction. We will only add here that to get a corresponding percentage of chlorine, 56.67, from the presence of the heptachlor hemiether, there must have been 25 per cent of this impurity.

Properties of Octochlororthobenzoquinhydrone.—It crystallizes in shining, black needles, which effervesce easily, becoming dull and of a dark-purple color. At 70° it turns yellow, probably from the formation of heptachlororthoquinopyrocatechin hemiether, and then melts to a red liquid at about 160°. It dissolves in ethyl or methyl alcohol, chloroform, benzene, toluene or nitrobenzene, but seems to be decomposed by solution, as is to be expected from its analogy with the paraquinhydrone. This decomposition seems less complete when the solvent is chloroform, benzene or toluene than with the alcohols or nitrobenzene, but this is probably due to the fact that the quinhydrone is formed again more easily from its constituents in the first set of solvents than in the

last. The treatment with nitrobenzene yields three products, probably the following: a white one, tetrachlorpyrocatechin; a red one, a mixture of tetrachlororthoquinone and the red ether $C_6Cl_4O_2C_6Cl_2O_2$; and a yellow heptachlororthoquinopyrocatechin hemiether.

Heptachlororthoquinopyrocatechin Hemiether, $C_6Cl_4OHOC_6Cl_3O_2$. —This substance was made by mixing hot solutions of equal parts of tetrachlororthoquinone and tetrachlorpyrocatechin in small amounts of chloroform and allowing the mixture to remain hot for about half an hour. Hydrochloric acid was given off and the yellow product deposited as the solution cooled, with an additional amount on evaporation. Chloroform with tetrachlororthoquinone alone gave no reaction. The yellow product was purified by crystallization from hot chloroform, or ligroin, for, although only slightly soluble in the latter when hot, it is insoluble in it when cold. It was dried *in vacuo* for analysis.

I. 0.1489 gram substance gave 0.1735 gram CO_2 and 0.0866 gram H_2O.

II. 0.1398 gram substance gave 0.3094 gram AgCl.

III. 0.1642 gram substance gave 0.3614 gram AgCl.

IV. 0.1716 gram substance gave 0.3770 gram AgCl.

V. 0.1836 gram substance gave 0.4056 gram AgCl.

VI. 0.2048 gram substance gave 0.4491 gram AgCl.

	Calculated for $C_6Cl_4OHOC_6Cl_3O_2$.	Found. I.	II.	III.	IV.	V.	VI.
C	31.47	31.78	...	...	...	...	...
H	0.22	1.24	...	...	...	...	...
Cl	54.31	...	54.72	54.42	54.32	54.63	54.22

The specimen used in VI. was crystallized from ligroin, the others from chloroform.

The molecular weight was determined by the boiling point method.

I. 0.1030 gram substance dissolved in 37.5 grams C_6H_6 gave $\Delta = 0.°017$.

II. 0.3167 gram substance dissolved in 32.8 grams C_6H_6 gave $\Delta = 0.°055$.

	Calculated for $C_6Cl_4OHOC_6Cl_3O_2$.	Found. I.	II.
Mol. wt.	457.5	421.7	458.1

Properties of the Heptachlororthoquinopyrocatechin Hemiether.—It crystallizes with some difficulty from chloroform in yellow scales, but in the earlier crystallizations of the impure substance good-sized square blocks were also observed. It decomposes on melting, as shown by its turning red, and the highest temperature at which we have observed these phenomena is 214°, but a specimen melting, or, rather, decomposing, at a much lower point, gave good results on analysis. The decomposition with reddening takes place very easily, in fact, slowly and partially, by mere exposure to the air and light, and more rapidly by heating, so that it is easy to see that the melting point would be very much influenced by the way in which the heat was applied. To study this reaction more carefully, 1.0782 grams of the substance were heated to 110°–140°. At first the loss was rapid, but after about half the theoretical amount of hydrochloric acid had been given off, the action became very slow, and was finally stopped after 8 weeks, although the weight was not absolutely constant. The residue weighed 1.0126 grams instead of the 0.992 gram expected from the reaction:

$$C_6Cl_4OHOC_6Cl_3O_2 = C_6Cl_4O_2C_6Cl_2O_2 + HCl.$$

The loss, therefore, is 76.28 per cent of the theoretical. It is hard to understand, with the formula ascribed to this substance, why the loss should not be quantitative and rapid. Ethyl or methyl alcohol or ether (unpurified ether containing some alcohol) decomposes it with reddening. After one failure to get a quantitative yield of the red ether by heating the compound, we tried the action of ethyl alcohol on it in hope of a better result, but the loss in this case was only 66.67 per cent of the theoretical and the red ether was contaminated with a soluble impurity, pointing to a secondary reaction. With methyl alcohol the amount of impurity seemed to be even larger. It is soluble in chloroform or benzene; essentially insoluble in cold, slightly soluble in hot ligroin; slightly soluble in nitrobenzene. Chloroform stood with it in the cold for over a month with no signs of any reaction, and this solution could even be boiled for a short time with-

out much decomposition. Cold water did not dissolve it, but on long standing with it took on the purple color of a solution of chloranilic acid. Strong sulphuric acid showed no reaction with the heptachlor compound in the cold but, on warming, gave a dark-green, almost black color. Sodic hydrate also turned the hemiether black, forming a yellowish-green solution, though the amount dissolved was very small.

Hexachlororthoquinomethylmonohemiacetalpyrocatechin Ether, $C_6Cl_4O_2C_6Cl_2O(OCH_3OH)$.—This substance has been described by MacLaurin and one of us,[1] but we have succeeded in improving the method of preparation, so that it can now be made quickly and easily. For this purpose the red ether,[2] $C_6Cl_4O_2C_6Cl_2O_2$, was boiled with methyl alcohol in a flask with a return condenser for a few minutes, the hot liquid was then poured off and replaced with fresh methyl alcohol and this process repeated until the ether was converted entirely into its hemiacetal, which took place in less than an hour. The product was nearly pure and the yield not far from quantitative. This method is, therefore, better than letting the ether stand in the cold with methyl alcohol, as recommended before. It was purified by crystallization from a mixture of equal parts of benzene and ligroin until it showed the constant melting point 198°. During the crystallization it was noticed that at first rhombic plates were formed, which, on the third crystallization, were converted into the characteristic clusters of needles. This phenomenon was observed only with specimens prepared from the red ether. To be sure that one product was the hemiacetal a sample was analyzed and gave 47.34 per cent Cl instead of 47.01.

Hexachlororthoquinomonomethylacetacetalpyrocatechin Ether, $C_6Cl_4O_2C_6Cl_2O(OCH_3OC_2H_3O)$.—This substance was prepared by MacLaurin and one of us,[3] but on the strength of a single analysis a different composition was ascribed to it. One of the principal observations which led to a wrong conclusion in regard to this substance was the formation of a red product, supposed to be the ether, $C_6Cl_4O_2C_6Cl_2O_2$, and to constitute an

[1] THIS JOURNAL, **38**, 150 (1907).
[2] *Ibid.*, **37**, 12 (1907).
[3] *Ibid.*, **38**, 153 (1907).

intermediate stage in the reaction. Our later work has shown that this red substance is tarry and easily soluble in benzene, so that it cannot be the ether, and also that it was not formed in nearly so large amount as was supposed at first.

The acet compound was best prepared by warming the hemiacetal melting at 198° with acetic anhydride on the steam bath for two hours, and allowing the hot liquid to cool. The crystals thus obtained were especially pure. An additional amount of somewhat poorer quality was obtained by evaporating off the anhydride from the remaining solution. The purification was effected by crystallization from equal parts of benzene and ligroin until it showed the constant melting point 220°.

The same product was obtained by heating the hemiacetal with acetic anhydride until all the anhydride had evaporated, or by heating it for 20 minutes and then removing the excess of anhydride with a blast of cold air. It was dried *in vacuo* for analysis.

I. 0.2925 gram substance gave 0.3930 gram CO_2 and 0.0430 gram H_2O.

II. 0.1748 gram substance gave 0.3034 gram AgCl.

III. 0.1697 gram substance gave 0.2949 gram AgCl.

This is the analysis given in the paper by MacLaurin and one of us.

	Calculated for $C_6Cl_4O_2C_6Cl_2O(OCH_2OC_2H_3O)$.	I.	Found. II.	III.
C	36.38	36.64	...	...
H	1.21	1.63	...	...
Cl	43.03	...	42.92	42.49

The substance forms masses like a cauliflower of a lighter yellow color than the hemiacetal and melts at 220° to a light-brown liquid. MacLaurin found 215°.

Attempts to convert this acet compound into the phenylhydrazone did not lead to the desired result for, although a reaction seemed to take place, it was evidently not the simple replacement of oxygen which we had expected.

Hexachlororthoquinomethylhemiacetalpyrocatechin Ether, $C_6Cl_4O_2C_6Cl_2(OCH_2OH)_2$.—This substance, which melts at

218°, was discovered by MacLaurin and one of us,[1] but no convenient way was found for preparing it. We have worked out the following method, similar to that used by Shaffer and one of us[2] with the bromine compound, by which it can be made in a few minutes instead of several months; but, unfortunately, this was done at the very end of the year, when no time was left for the study of the material thus obtained. The tetrachlororthoquinopyrocatechin ether was mixed with a methyl alcohol solution of sodic methylate (made by treating 50 parts of the alcohol with one of sodium), which was added slowly until the ether just went into solution. The mixture was then barely acidified with sulphuric acid, more methyl alcohol added, and the whole heated. The sodic sulphate was filtered out of the hot solution, and, as the filtrate cooled, it deposited white crystals of the desired product, mixed with a small amount of a yellow impurity, apparently the monohemiacetal, melting at 198°. Four crystallizations from hot methyl alcohol were sufficient to purify it, as shown by the constant melting point 218°.

Two sets of preliminary experiments may be described here. Tetrachlororthoquinone, mixed with half its weight of acetophenone, turned yellow after standing 2 or 3 days. The product, washed with ligroin and crystallized from a mixture of benzene and ligroin, melted at 281°, contained 42.90 per cent of chlorine, and was essentially insoluble in alcohol, even when hot. The tetrachlororthoquinone, therefore, did not behave like the tetrabromorthoquinone under these conditions, as that gives[3] the ether $C_6Br_4O_2C_6Br_2O_2$, its reduction product, $C_6Br_4O_2C_6Br_2(OH)_2$, and the hemiether $C_6Br_4OHOC_6Br_3O_2$, whereas our product melts too high for the hemiether and too low for the complete ethers, and contains 8 per cent less chlorine than they do. This is the more unexpected as MacLaurin and one of us[4] obtained, from the action of acetone on the tetrachlororthoquinone, three products which seemed to correspond to the bromine compounds

[1] THIS JOURNAL, **38**, 154 (1907).
[2] *Ibid.*, **34**, 463 (1905).
[3] *Ibid.*, **35**, 170 (1906).
[4] *Ibid.*, **37**, 10 (1907).

mentioned above. These experiments will be continued in this laboratory.

If tetrachlororthoquinone (or pyrocatechin) was heated with fuming nitric acid to which a little strong hydrochloric acid had been added and the heating was stopped when a reddish tar had collected at the bottom, a substance was obtained which was purified as follows: The mixture was allowed to stand overnight and then, after diluting it with water, was heated on the steam bath with frequent stirring, which converted the red tar to a yellow solid. This was washed with alcohol and crystallized from a mixture of about 3 parts of alcohol to 2 of benzene, or from glacial acetic acid, until it melted at 146°–147°. The product obtained in this way consisted of long, yellow prisms mixed with yellow rhombic plates, and therefore we feel no certainty that it was pure. Two preliminary analyses were made, however; one, mostly prisms, gave Cl 62.72 per cent, the other, which contained more plates, Cl 61.83 per cent. More work is obviously necessary before its nature can be determined, but it shows a strong resemblance to a substance obtained by MacLaurin and one of us[1] by the long continued action of chlorine in acetic acid solution on tetrachlorpyrocatechin. This melts at 146°–147°, crystallizes sometimes in yellow needles, sometimes in yellow plates, and contains 63.06 per cent of chlorine. An abnormal quinone, $C_6Cl_2HO_2$, contains Cl 62.84, but it would be unsafe to assign this formula to either of these products upon our present data. The formula $C_6Cl_4O_2$, which the substance would have if it corresponds to the bromine compound,[2] contains Cl 60.88. In preparing our yellow product success depends on stopping the boiling with nitric acid at just the right point. If stopped too soon, the product remains obstinately tarry; if carried on too long, it is converted almost completely into oxalic acid. We can give only two indications of the point at which the action should be stopped: a red tar should appear at the bottom of the liquid and the chlorine should have ceased to come off rapidly from the mixture, but even with these

[1] THIS JOURNAL, **37**, 19 (1907).
[2] *Ibid.*, **35**, 184 (1906).

indications the point was so hard to determine that we could not invariably succeed in preparing the yellow product. On one occasion a white substance was also obtained, which burnt with a smoky flame and gave a test for halogen when heated on a copper wire. This may be analogous to the white acid obtained from the tetrabrompyrocatechin in a similar way by Russe and one of us.[1] The work will be continued in this laboratory.

CAMBRIDGE, MASS.,
August 16, 1907.

ON SOME CUPRAMMONIUM SALTS. VI.[2]

BY DAVID W. HORN AND MINNIE A. GRAHAM.

The object of this paper is to describe a case of isomerism met with in the course of a study of cuprammonium salts. Up to the present, isomerism has not been known in this group of compounds.

The isomeric substances in question are represented by the formula

$$Cu(OOC)_2.2NH_3.$$

One of these was described in a previous paper.[3] It has since been found to be characterized by exceptional chemical inactivity under certain circumstances. It can be kept in an atmosphere of dry ammonia gas for at least one month without change in weight, and it remains unchanged under liquid ammonia throughout several hours. In other words, it acts as a *saturated* compound toward ammonia. For the sake of clearness, this oxalate will be referred to hereafter as the α-compound.

This apparent saturation was unexpected and suggested the existence and preparation of an *unsaturated* compound of the same composition. The pentammine oxalate described in a previous paper undergoes dissociation, under the proper conditions, as follows:

$$Cu(OOC)_2.5NH_3 \rightleftarrows 3NH_3 + Cu(OOC)_2.2NH_3.$$

[1] THIS JOURNAL, **35**, 186.

[2] Read in abstract at the meeting of the American Chemical Society at Toronto, June 28, 1907.

[3] THIS JOURNAL, **35**, 275 (1906).

Since dissociations are reversible, the diammine oxalate prepared in this way should differ from the α-compound in that it should react readily with ammonia. We shall refer to such an unsaturated diammine oxalate as the β-compound.

We prepared the β-diammine oxalate from the pentammine salt and the pentammine oxalate for this purpose from the monammine oxalate.

The monammine oxalate, we find, is best prepared as follows: 7.6 grams of air-dried copper oxalate are warmed with 45 cc. of ammonia water of sp. gr. 0.9 until solution is complete. The solution is poured gradually and with constant stirring into 2250 cc. of water. The diluted solution thus obtained is set aside in evaporating dishes. The monammine salt separates out after the lapse of from 1 to 3 days, depending upon the area of the free surface of the evaporating liquid. The salt is dried in the air. The following analyses served for identification:

Weight taken for analysis. Grams.	Volume acid neutralized by the ammonia. cc.	Percentage ammonia found. Per cent.	Percentage calculated for $Cu(OOC)_2.NH_3$. Per cent.
1.5038	43.64	9.92	10.11
0.6951	20.49	10.06	...

When the monammine salt is placed in dry ammonia gas at 1 atmosphere pressure and ordinary temperatures, the color begins to change at once and the weight increases. After some time, the increase in weight ceases. The following figures show that the reaction is to be represented by the equation

$$Cu(OOC)_2.NH_3 + 4NH_3 \rightleftarrows Cu(OOC)_2.5NH_3:$$

Weight monammine salt taken. Grams.	Time in ammonia gas. Hours.	Percentage gain in weight.	Percentage calculated for above equation.
0.4987	96	38.98	40.46
0.2624	48	38.87	...
2.3091	72	39.65	...
2.3879	15	39.08	...

The first attempts to dissociate the pentammine oxalate into the β-compound were made at $+90°$. It was heated, in a boat, in a tube that was sealed at one end and was closed at the other by a rubber stopper with one perforation, through

which passed an L-shaped delivery tube so arranged that its outer end dipped just beneath the surface of mercury.

The product obtained by heating under these conditions to constant weight had the composition of a diammine oxalate as is shown by the following analyses:

Weight taken for analysis. Gram.	Volume of acid neutralized by the ammonia. cc.	Percentage of ammonia found.	Percentage calculated for $Cu(OOC)_2.2NH_3$. Per cent.
0.2032	10.73	18.03	18.38
0.1670	9.29	18.98	...
0.4566	23.72	18.14	...

This product was sky-blue, whereas the α-compound has a brilliant sapphire color. The sky-blue color soon changed to darker blue and purple shades when the product was placed in dry ammonia gas, indicating addition was taking place under the same conditions under which the α-compound remains unchanged. Differences in the state of subdivision might be considered as the cause of the difference in color, and differences in the properties of the surfaces of the substances, as the cause of the different behavior toward ammonia gas. To determine whether the differences were superficial or deeper seated, the specific gravity of the α-compound and of the product obtained at $+90°$ was determined.

We used specific gravity bottles of 2, 25 and 50 cc. capacity. Since the diammine oxalates are slowly decomposed by water, the specimens were weighed in alcohol, xylene or nitrobenzene. The most concordant results were obtained in the nitrobenzene. The values for the specific gravity of the nitrobenzene are given in the first column of the following table; for that of the α-compound in the second column; and for that of the product obtained at 90° C. in the last column, first three numbers:

Nitrobenzene D^{25}_4.	α-Compound D^{25}_4.	Dissociation product D^{25}_4.
1.2017	2.308	2.224
1.2015	2.308	2.225
1.2016	2.305	2.235
1.2015	2.303	...
1.2014	2.304	2.212
1.2015	2.305	2.227

The difference between the average values for the sp. gr. of the α-compound and for the dissociation product indicates more than a superficial difference between these two substances.

To avoid, as far as possible, any isomerization that may occur at higher temperatures, the dissociation was accomplished at ordinary temperatures. The method consisted in placing the pentammine salt in a desiccator over sulphuric acid until it no longer changed in weight. In the following table are given the successive weights of a specimen of the pentammine salt kept over sulphuric acid. The substance was enclosed in a weighing tube shaped like an Erlenmeyer flask. A rounded glass rod with which the powder was frequently and thoroughly stirred was kept in the weighing tube throughout the experiment.

It has been shown in the preceding paper that the pentammine salt passes to a diammine salt under these conditions. The question whether or not constant weight is finally obtained over sulphuric acid is answered in the following experiment: The pentammine salt used had been prepared for some time and had already lost some of its ammonia. The last four figures show that the final product has an almost negligible dissociation tension of ammonia at the temperature of the experiment, *i. e.*, that of the room:

Time in hours.	Weight in gram.	Loss in weight per hour.
0	0.5952	....
4	0.4864	0.0272
8	0.4843	0.0005
22	0.4764	0.0005
46	0.4743	0.0001
71	0.4733	0.00004
95	0.4732	0.000004

In preparing larger quantities of the diammine salt, amounting to five grams of more, the pentammine salt was put in a mortar, with its pestle, in a desiccator some 24 cm. in diameter and containing 250 cc. sulphuric acid of sp. gr. 1.84. The mortar was removed frequently and the material in it ground and mixed with the pestle.

The product obtained by this method adds ammonia rapidly when placed in an atmosphere of that gas. Because it has the same composition as the α-compound, yet behaves as an unsaturated body toward ammonia, we shall refer to it as the β-compound. The last two numbers, column 3, preceding table, are the specific gravities of specimens of it.

In order to make a final test of the view that we had here isomeric substances, and that one of these was capable of passing over into the other, we took advantage of the method of determining transition temperatures, already referred to.

In some preliminary experiments made in a melting point tube, the product obtained at $+90°$ had been found to change from sky-blue to light green at about $+180°$, and to brown at about $+220°$. The α-compound was found to change from sapphire to dark, olive-green when held in a paraffin bath at about $+215°$. When examined by the transition point method neither the α- nor the β-compound exhibited any change, whatever below $+150°$ at 3 cm. pressure.

The two substances were then examined by this method at the same pressure at temperatures above $+150°$ C. For this purpose, one end of a long piece of glass tubing was sealed and blown into a small bulb. A thermometer, graduated into tenths and reading from $+150°$ to $+206°$, was introduced so that its bulb came within the glass bulb at the end of the tubing. Enough α-oxalate was then poured in to cover the bulb of the thermometer, and the tube was clamped in a vertical position. The upper end of the glass tubing was then closed by a rubber stopper with one perforation, through which passed an L-shaped delivery tube, which was connected with a filter pump and a manometer. After the pump was started the glass bulb containing the oxalate surrounding the bulb of the thermometer was immersed in a paraffin bath maintained at $+202°$ to $+204°$.

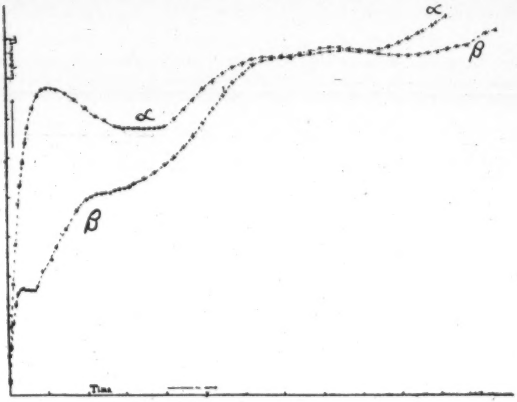
After the completion of the experiment with the α-oxalate, it was repeated under exactly the same conditions with the β-oxalate. The results of the two experiments are given in the following table:

Time in minutes.	Thermometer readings		Time in minutes.	Thermometer readings		Time in minutes.	Thermometer readings	
	α.	β.		α.	β.		α.	β.
0	161.4	161.3	22	187.2	180.7	62	194.7	194.5
0.5	166.9	164.8	23	187.1	180.8	64	195.0	194.6
1	171.2	167.2	24	187.0	180.9	66	195.1	194.7
1.5	175.2	169.1	25	187.0	181.1	68	195.0	194.8
2	179.3	170.2	26	187.0	181.4	70	194.8	194.9
2.5	181.2	170.6	27	187.0	...	72	194.6	194.8
3	183.5	170.7	28	187.0	181.9	74	194.6	194.6
3.5	185.5	170.6	29	187.0	...	76	194.8	194.4
4	187.0	170.6	30	187.0	182.5	78	195.1	194.3
4.5	...	170.6	31	187.0	...	80	195.5	194.2
5	189.0	170.6	32	187.2	183.3	82	195.9	194.2
5.5	...	170.6	34	187.9	184.1	84	196.4	194.2
6	190.2	171.0	36	189.0	185.1	85	196.6	...
7	190.8	172.6	38	189.8	186.2	86	...	194.3
8	191.0	...	40	191.0	187.5	87	197.1	...
9	191.0	173.7	42	191.7	189.0	88	197.4	194.4
10	190.9	174.9	44	192.5	190.3	90	198.0	194.7
12	190.5	176.8	46	193.1	191.6	92	...	194.9
14	189.8	178.7	48	193.6	192.6	94	...	195.1
16	189.0	179.8	50	194.0	193.4	98	...	195.4
17	...	180.1	52	194.2	193.9	100	...	195.6
18	188.2	180.3	54	194.1	194.1	...	...	...
19	...	180.4	56	194.3	194.2	...	...	...
20	187.8	180.5	58	194.1	194.3	...	...	...
21	...	180.5	60	194.5	194.4	...	...	...

The data in this table are represented graphically in the following figure.

The curves indicate clearly that the two substances are quite different. The principal differences in their behavior may be seen at a glance. The five transition temperatures are very well marked, considering that the bath was maintained throughout at a temperature so far above them. But this was necessary in order that the two sets of data should be comparable. The irregularity of the curves about +194° is due to the relative violence of the dissociation at this temperature. The solid was thrown in considerable quantities to the upper part of the tube where it often lodged temporarily and always cooled before it fell back into the region

about the bulb of the thermometer. In the first experiment, the material that lodged was shaken down at times by tapping the tube with a pencil, and this caused fluctuations that did not occur in the second experiment where the tapping was avoided. Each of the 5 transition temperatures was confirmed in a separate experiment.



Under the given conditions, the sapphire α-compound yields a deep olive-green product at about $+187°$, while the sky-blue β-compound yields a pale Nile-green product at about 171°. Both the α- and the β-compound yield a dark chocolate-brown body at about the same temperature, $+194°$, and the product from the one cannot be distinguished by its appearance from that from the other.

We did not have sufficient time to determine the composition of these products, but it is our opinion, in view of the behavior of the diammine sulphate when heated, that the two green products are monammine oxalates, and that the transition point occurring at about 180° in the curve of the β-compound corresponds to the transformation of one monammine oxalate into its isomer. This idea is in accord with the superposition of the two curves at about $+194°$ and with

the apparent identity of the brown products finally obtained in both cases. The two green (monammine) oxalates will be examined when the work can be resumed.

It will be recalled that the possibilty of a partial isomerization of the β- into the α-compound under the conditions stated was suggested. This idea was confirmed with a preparation of the diammine salt obtained by heating the pentammine oxalate in the vacuum of a filter pump gradually to 100° and maintaining it at that temperature for some 4 hours. This product, if there had been no isomerization, should have given the heating curve of the β-compound, whereas, if isomerization had occurred, it should have given the curve of the α-compound. The following data were obtained. The transition temperature is +187°.2.

Time in min.	Temp. C.	Time in min.	Temp. C.	Time in min.	Temp. C.	Time in min.	Temp. C.
0	161.5	7	185.7	17.25	188.7	28	187.2
1	164.4	8	186.9	20.5	188.5	29	187.2
2	169.2	9	187.6	21.75	188.2	30	187.2
3	174.1	10	188.1	24	187.2	31	187.2
4	178.4	11	188.5	25	187.2	32	187.2
5	181.7	13	188.7	26	187.2	33	187.2
6	184.2	15.5	188.8	27	187.2	34	187.2

This experiment shows that the β-compound must be the labile isomer and the α-compound the stable one, and that the former may be transformed into the latter when heated to about +100°.

The following table contains a summary of the properties of these two isomers.

α or Stable Form.	β or Labile Form.
Saturated toward ammonia	Unsaturated toward ammonia.
Crystalline[1]	Thus far obtained only in amorphous condition.
D_4^{25} 2.305.	D_4^{25} about 2.230.
Intense sapphire in color.	Sky-blue in color.
Dissociates into a deep olive-green compound at 3 cm. pressure and about +187°.	Dissociates into a pale Nile-green compound at 3 cm. pressure and at about +171° C.
	Passes more or less completely into the α-form at about 100° C.

[1] THIS JOURNAL, 28, 275 (1906).

There are indications of isomerism in diammine salts of other dibasic acids; for example, the *saturated* diammine carbonate is already known.[1]

ON THE THEORIES OF CATALYSIS: A REPLY TO JULIUS STIEGLITZ.

[EIGHTH COMMUNICATION ON CATALYSIS.]

By S. F. Acree.

Mr. Stieglitz's reply in the March number of This Journal absolutely confirms the accusations which I made against him in January. The real cause for Stieglitz's December note was his desire to hold the field of catalysis for himself and to get all possible credit for clearing up the large number of important problems in this field. This desire is so great that it lead Stieglitz to make *false charges* against me in December, and now leads him to *depreciate unjustly* the work of others, in order that he may get all the more credit. The field is large enough for the several workers, Kastle, Bredig, Euler, Goldschmidt, Lapworth, Acree, Stieglitz and others, and Stieglitz has no claim over them. I have been working on catalytic phenomena since 1899, especially on problems in tautomerism.[2] I shall endeavor to avoid a conflict with the specific problems of others, unless these problems are a legitimate part of our work. I shall always try to credit others for their work, a thing which Stieglitz has not done.

I wish to have it understood that my reply of January was most emphatically not a "tu quoque" but a "tu solus" answer. If Stieglitz had shown any kind of decent consideration in 1904, or in our correspondence of last summer, for my work and ideas and those of others, we should not now be engaged in this controversy; it was his selfish attitude that made it

[1] This Journal, **39**, 215 (1908).

[2] The ideas involved in the hydrolysis of alkyl halides, of the urazole O-esters by acids, in the catalytic change of O-esters of urazoles, amides, etc., into the N-esters by alkyl halides, in the study of the action of various salts on the alkylation reactions and in other problems in catalytic condensations by alcoholates and alkalies, have been an *absolutely essential part of our work on tautomerism*, as is shown in Brunel's Dissertation, 1906; This Journal, **37**, 71; **38**, 1; **38**, 259, 335–348, **39**, 226; and in two articles soon to appear in This Journal.

necessary for me to discuss in detail in my September and December articles the ideas of all the principal workers in catalysis, including Stieglitz; it was his continuation of this attitude in his December note and in his correspondence that made me enter my vigorous protest in January.

I charged Stieglitz then, as I do now again, with having *deliberately misrepresented* the facts in his December note[1] and in this last reply in his attempt to cast reflections on my honesty and rob me of credit for new and independent ideas in catalysis and especially of priority over him in the theoretical and experimental proof that the second and third "so-called" laws of catalysis do not always hold, and I claim now again that no honorable chemist would have ignored, as did Stieglitz, the work of Kastle,[2] Euler,[3] Bredig,[4] Lapworth,[5] and myself.[6]

The work of these chemists, *together*,[7] anticipated practically all of the ideas put forward by Stieglitz in 1904. Stieglitz should have pointed out the good and bad points in 1904, as I did in my September article and as Stieglitz has now been forced to do by my arraignment of his methods. He chose, instead, in 1904, and in December and now again, to ignore, hide or misrepresent the work of others, and make it appear that he alone is responsible for the recent important developments in catalysis. I use the words "ignore, hide or misrepresent" advisedly because Mr. Stieglitz repeatedly fails again in his last article to credit others with priority in matters which he presents as new and tries to lead his readers to believe that certain theories of catalysis are contrary to the truth.

[1] THIS JOURNAL, **38**, 743.

[2] *Ibid.*, **19**, 894. Especially see P. Am. Assn. Adv. Sci., **47**, 238. for an abstract of the original article, which was never published in full, and which Prof. Kastle kindly sent me at my request.

[3] Z. physik. Chem., **36**, 405. 663; **40**, 501; **47**, 356; Z. physiol. Chem., **52**, 146.

[4] Z. Elek. Chem., **9**, 118; **10**, 586; **11**, 528.

[5] Mellor's "Statics and Dynamics," p. 289.

[6] Acree and Hinkins: THIS JOURNAL, **38**, 370. See also *Ibid.*, **37**, 410; **38**, 258, 489, 746; **39**, 145, 226. 300.

[7] In Professor Acree's original manuscript of his January article the sentence on page 151, last two lines, read: "We see then that Kastle, Euler, Acree and Bredig together had priority over Mr. Stieglitz, etc." The word "*together*" was changed to "*all*" through an error of the assistant editor.—EDITOR.

Mr. Stieglitz's statement that I proclaimed Kastle as "the original discoverer of the theory of oxonium salts" is not correct. I invite all chemists to read the pp. 147, 149, 156, cited by Stieglitz, and also to read THIS JOURNAL, **38**, 298, 335–339, to learn the truth. Kastle (1898) deserves credit for priority over Collie and Tickle (1899) and Baeyer and Villiger (1901) for the idea that ester hydrochlorides are tetravalent-oxygen compounds, but not for the idea of their ionization. I inserted the words "Kastle's salt" to make it clear to my readers that we call these ester hydrochlorides, today, following Collie and Tickle, *salts*. Although Kastle did not call the ester hydrochlorides *salts* he did call the amide hydrochlorides *salts*[1] and pointed out that the hydrolysis of amides and esters[2] is "essentially the same in kind." We see then that *Kastle preceded Stieglitz just six years* in proposing the views that the catalysis of amides ("nitrogen compounds" analogous to imidoesters) is due to the hydrolysis of the *amide salt*, which has the ammonium-salt structure of Stieglitz's *imidoester salts*. Kastle did not take up the question whether these salts undergo changes through their molecules or ions.

Furthermore, Mr. Stieglitz has deliberately misled his readers concerning Kastle's theory (1) by quoting only from a paper of 1896, after I had quoted Kastle's 1898 paper, *the only one presenting his views fully on catalysis*, and (2) by deliberately making postulations and perversions of the facts and spirit of Kastle's theory, of my 1902 work, by making a mistake in Lapworth's work, etc. I shall point out these and many other errors in my next article on the *Theories of Catalysis*, in which I shall try to deal more fairly with the work and ideas of my various colleagues than Mr. Stieglitz has done.

Mr. Stieglitz, in discussing my work of 1902, has wasted

[1] His exact words are: "In the catalysis of nitrogen compounds it is only necessary to assume the usual change of valence from three to five..... The amides of the carbonic acids, as is well known, are readily transformed into ammonium salts under the influence of acids; and for reasons similar to those already discussed for the hydrolysis of ethers. A few unstable salts of these amides have been isolated which are of just such a nature as is demanded by the hypothesis, etc., etc." (Manuscript, pp. 19. 21.)

[2] THIS JOURNAL, **39**, 147.

much valuable space in asking a question,[1] "Why was this effort made to force the term *salt* in this sense into his views against the printed evidence?" and in giving himself an answer that pleases him. The real answer, "obvious to every man of even an average intelligence who can read English" (p. 408), is given by the *printed evidence*, my equations,[2] which show that I assumed the compound enz. $C_6H_{11}O_5Ac$ to *ionize* as a *salt* into enz. $C_6H_{11}O_5$ and Ac, and the compound enz. $C_6H_{11}O_5(OH)$ as a *base*[3] into enz. $C_6H_{11}O_5$ and OH:

$$C_6H_{11}O_5OH + HAc + \text{enz.} \rightleftarrows$$
$$\text{enz. } C_6H_{11}O_5OH + H + Ac \rightleftarrows$$
$$\text{enz. } C_6H_{11}O_5 + OH + H + Ac \rightleftarrows$$
$$\text{enz. } C_6H_{11}O_5Ac + H_2O \rightleftarrows$$
$$C_6H_{11}O_5Ac + \text{enz.} + H_2O.$$

Can anything be plainer? I had no occasion to call them *salts* or *bases* in 1902, as Stieglitz was not then *haggling over words*. I believe that my readers see that the *idea* of "acceleration through salt and ion formation" is the central one of my equations of 1902, and that was what I wished to show in January. I shall discuss this in detail in my next article on the *Theories of Catalysis*.

Mr. Stieglitz now tries by *deliberate misquotation* to make it appear that I misquoted him in giving his fundamental points. I only wish that the readers would look through our original papers to see how flagrantly Mr. Stieglitz *misrepresents* me in these quotations. I give his version of my words and my real sentences in parallel columns:

[1] THIS JOURNAL, **38**, 406.

[2] *Ibid.*, **38**, 372.

[3] By an oversight this substance was called "enzyme-glucose *salt*" in January (p. 149).

(*a*) Mr. Stieglitz's quotation from me (p. 409): "Mr. Acree's version (claiming to give my fundamental principles: *vide* the original, THIS JOURNAL, **39**, 146, for the exact phraseology): 'Mr. Stieglitz says (p. 744): "In that address, the first vital and decisive step was taken to depart from the old idea that.... the catalytic agent must appear to act by its presence simply and not to form a compound in any quantity with any of the components....." ' "

My (Acree's) real quotation, giving, as I see them, the fundamental principles worked on by Stieglitz: see THIS JOURNAL, **39**, 146. "Mr. Stieglitz says (p. 744): 'In that address the first vital and decisive step was taken to depart from the old idea that .... the catalytic agent must appear to act by its presence simply and not to form a compound in any quantity with any of the components. ..... The most fundamental fact concerning acids was recalled, the fact that they have the power to form salts with bases and oxides. .... We .... could *prove our point that the acceleration is .... due to salt and ion formation.*' "

Bearing in mind that I was discussing the first "so-called" law of catalysis I leave it to my readers to judge whether I give in the above paragraph (*a*) and in his quotation (*b*) the essence of Mr. Stieglitz's ideas of 1904, on page 744; these, and not his (*my!*) ideas of December, 1907, or later, were the ones under discussion.

In his section (*c*), p. 410, he *deliberately misrepresents* the issue between us. By giving the following sentence of my section (*b*) he makes it appear that I wished to commit him as holding, in December, 1907, the view that the second and third laws of catalysis always hold. *I made there* (p. 153, January) *the crucial point that he did not have in 1904 the views that these laws do not always hold.* Of course, he knew, in December, 1907, that the second and third laws do not always hold because I had published these facts in THIS JOURNAL in April and September, 1907, and had written Stieglitz of the work, and Abel[1] and Euler[2] had reached the same conclusions from theoretical grounds.

[1] Z. Elek. Chem., **13**, 555.
[2] Z. physiol. Chem., **52**, 146.

(*b*) Stieglitz's ideas which appeared, *not in 1904*, but in December, 1907, after he had read my work of September, 1907, given in the opposite column: "..... *in the case of very weak bases*, like methyl acetate, *when the amount of salt formation lies beyond the scope of our methods of experimental measurement.* For all other cases, the three fundamental principles consequently do not apply and in *no case* do they apply rigorously."

My words of September, 1907, of which Stieglitz's ideas in the opposite column, published *later* in December, 1907, look very much like a copy. Page 311: In comparing esterification and oxime hydrolysis: "In this reaction (esterification)[1] the *equilibrium is not disturbed appreciably*"[2] because[1] "little of the hydrogen ions unites with either organic acid or ester, whereas ..... nearly all the hydroxylamine exists in the form of cations." (*And the equilibrium is disturbed.*)[1] Again, on page 349: "These so-called laws are not laws at all, but apply only to certain special cases....." They cannot be used to make predictions concerning all catalytic reactions, but *are only approximate*[2] expressions of special reactions." Again on page 351: "It (the second law)[1] can only hold in those cases in which the base is so weak that *only a trace of the salt is formed*[2]....." Examples could be multiplied.

Mr. Stieglitz's repeated attempts in this last article to take credit from me by stating that he discarded the second and third laws in 1904 only show to what methods he will go to try to get a little more credit for himself; we notice that he never gives a direct quotation to bolster up his position. I invite every one to read his St. Louis paper for himself to see if I am too severe on him.

When now forced to do so by my arraignment, Mr. Stieglitz furnishes the necessary proof of the correctness of my charges

[1] Words inserted and left out for clearness and conciseness only: see the original.
[2] Italics are new for emphasis.

that the vital points in his 1904 paper and December note were not new, although he tries to hide his culpability by berating me in the same breath. In his 1904 paper he uses exactly the same formulas for the *intermediate*[1] ester and acid hydrochlorides and hydroxides that Kastle used in 1898. This idea of an intermediate compound, formed by the union of the catalyzing acid, base, etc., and the substance undergoing transformation, is the *vital idea* of catalysis, and one that Euler, Lapworth, Goldschmidt, Bredig, Acree and Stieglitz have also used.

Furthermore, Mr. Stieglitz now admits (p. 415) that "I (Stieglitz)[2] have never claimed that I was the inventor of the principle that *catalytic action is due to the formation of salts and their ionization*,[3] a principle that was most clearly and emphatically enunciated by Euler in 1901 as a hypothesis, without rigorous experimental proof, although with very good arguments." In other words, Acree was correct in pointing out in January (p. 146) that "Stieglitz's keynote, acceleration through salt and ion formation," was not original with him and is the same keynote that several others are using!

But Mr. Stieglitz did make himself appear to be "the inventor" of this "principle" by not referring to Euler in this connection in his 1904 paper, and thus failing to credit Euler with priority. It is this habit of hiding or ignoring the work of others for which I arraign Stieglitz. Since Stieglitz also gives priority to Euler and others for his (?) (Stieglitz's) (p. 418) ideas as to why the salts of weaker bases change into salts of stronger bases,[4] we see, as I claimed in January, that there is really not very much *new* in Stieglitz's *ideas*: his recently published experimental work, however, showing that imidoester cations are hydrolyzed, and *verifying Bredig's ideas*, is brilliant and that is really all for which he deserves credit.

[1] $\underset{H}{Cl}CH_2COOR$, $\underset{H}{Cl}CH_2COOH$, $\underset{H}{OH}CH_2COOR$.

[2] My word, for clearness only.

[3] Italics are mine, for clearness.

[4] That this is not a general rule is shown by the fact that in our oxime and hydrazone work the salt of a strong base, hydroxylamine, or phenylhydrazine, is changed into a salt of a very much weaker base, acetoxime, or acetonephenylhydrazone.

Mr. Stieglitz now confesses that the views of Bredig and Goldschmidt are correct (pp. 414, 415, 425). His excuse that he did not refer to Bredig's complex-cation hypothesis, practically identical with the one used by Stieglitz, myself, Goldschmidt and others "only on account of its being hidden in papers on different topics" is *strange* in view of the fact that the title of Bredig's paper was "Die Jodionen-Katalyse des Wasserstoffsuperoxyds." It was certainly a paper on catalysis, which all workers in catalysis should have read. Besides this I wrote Stieglitz all about these various pieces of work last summer and he read my *September* article, and yet he did not refer to Bredig in this connection in *December*, *January* or *February*. This only shows that even after Stieglitz knows of the prior work of others he fails to give them due credit until forced to do so by some such arraignment as my January article.

Even though Stieglitz cannot see, *after Bredig and Walton pointed it out*, the connection between ester catalysis and their quantitative proof of the catalysis of hydrogen peroxide by iodides *through the intermediate formation and decomposition of an iodoso ion*, some of us can; perhaps Mr. Stieglitz will be *willing* to do so in time. My chief reason for quoting this work in January was simply to show that Stieglitz's imido-ester-cation hydrolysis had been *preceded* by Bredig and Walton's proof of an analogous catalytic reaction through the formation of an intermediate *iodoso anion*, which work led them to postulate the theory of catalysis now used by Stieglitz, Goldschmidt, myself and others.

Mr. Stieglitz's most shameful misrepresentation is his sporadic attempt in his December note and in this last article to make it appear that my work on catalysis and my new ideas are simply a variation and *copy* of his own. Such an assumption is not only absurd but a "fabrication out of the whole cloth."

The equations and ideas used in my September and other articles are simply an expression of the mass law which I have used for several years in my work on tautomerism, reactions of alkyl halides, etc. *These equations did not originate with Stieglitz, but with Guldberg and Waage, and others, about forty years ago!*

I shall now, much against my will, point out some *absurd mistakes* which Mr. Stieglitz made in his St. Louis paper *in the very fundamental mass law and theory of ionization that he parades as the basis of all his work*, mistakes so great that if any one tried to copy them he would be led far away from the new things which I developed. On p. 279, in discussing the catalysis of imidoester hydrochlorides he says: "As the experiments were carried out in dilute solutions in which *the salts are practically completely ionized, it is obvious that it is the positive ion which is decomposing*[1] . . . . . " This is the evidence then given to us in 1904 to show that imidoester cations, and not the nonionized salt, are hydrolyzed! There is absolutely no word showing that he proved this beyond doubt by changing the relative concentrations of the imidoester cations and the undissociated salt by diluting the solution, or by suppressing the ionization with ammonium chloride, etc., and thus showing that *the mere trace of undissociated salt is not* the substance *hydrolyzed*. To point out to us now that this proved in 1904 that imidoester cations are hydrolyzed is too much for a shrewd man like Stieglitz to ask of us. How could I *copy* this kind of mistake and ever come to my *new* work showing that *it is the very trace of the undissociated hydrochloride of acetylchloraminobenzene that is decomposing*? How could I *copy* such mistakes and ever come to our proof that when alkyl halides react with the practically undissociated urazole acids *only the trace of urazole anions is concerned* to any extent? When I wrote to Mr. Stieglitz last fall about this mistake he assured me that he had carried out in 1904 the experiments I mentioned above. Then why did he not say so in 1904 in his paper? And knowing that I pointed out this mistake to him why does he *deliberately misrepresent* me in December and say that I copied from him, when he knows that I *corrected him*?

And then on p. 282 he has made a mistake[2] in Arrhenius' hydrolysis equation:

$$(Posit.\ Ester\ Ion) = \frac{K_{Base}}{K'} \times (Ester - y) \times (H').$$

[1] Italics are mine for emphasis.

[2] In his January article (p. 36) he does not make this mistake.

How can H' of hydrogen ions form y of salt without becoming $(H'—y)$, just as *Ester* becomes $(Ester—y)$? How can an acid neutralize a base and yet not change its concentration? Again I ask how can any one *copy* such mistakes and ideas and ever arrive at the absolutely new theoretical and experimental proof that, much of the H' being used up and $(H'—y)$ becoming small in comparison with H', the second and third laws of catalysis do not hold in such cases as the oxime work?

In view of his many mistakes in testing the theories of others, in view of his mistakes in the indicator work,[1] in view of the above mistakes in the fundamental points of his own work, in view of the fact that as late as 1904 he knew so little of calculus that he found it necessary to ask a colleague[2] to solve an equation so simple that the solution is given in Pierce's "Table of Integrals," used by Junior college students, it is evident that any one attempting to copy Stieglitz's immature ideas of 1904 and later would have been led into a hopeless mire and would never have discovered the new points brought out by me.

Still more questionable was Mr. Stieglitz's attempt in December to mislead an innocent chemical public, very few of whom can, or will, follow accurately this complicated question, into believing that "there is not one single new principle in Acree's paper." *The only things*[3] *that I claimed as new were the two new theoretical and experimental proofs that the second and third laws of catalysis do not always hold,* and, as I pointed out in January, Stieglitz had published, before my April and September articles, *nothing* bearing on this but that the second and third laws *do hold* in esterification work. I pointed out in January that Abel and Euler also have credit with me for these views. But Stieglitz did not point them out in 1904, and his attempt to rob me of these is still more astounding in the light of his January and February articles, in which practically all that he knows, *printed in two*

[1] See the next article in THIS JOURNAL.

[2] THIS JOURNAL, **31**, 463.

[3] *Ibid.*, **88**, 299, 300, 301, especially 335, 339, 342; and *Ibid.*, **39**, 152.

short paragraphs on pp. 56 and 62, is that the second and third laws do not always hold: *and this was written after he knew of my work showing that they do not hold.*

When forced to do so, Mr. Stieglitz now admits (p. 403) "as a welcome addition" my proof that in the rearrangement of acetylchloraminobenzene in the presence of hydrochloric acid we have a case of *pure catalysis* in which the second law does not hold, the velocity being proportional to the concentration of an undissociated salt and to the second power of the concentration of the hydrogen ions instead of to the first power as in esterification, etc. *In a footnote* (p. 412) he now calls my "second proof" of the nonvalidity of the second and third laws "very pretty." How can this "welcome addition" then be a copy of Stieglitz's work when he has done absolutely nothing like it, all of his reactions being those of ions or a free base? Mr. Stieglitz calls this "welcome addition" a "minor" case. Since it is analogous to the catalytic changes of phenylnitramine, phenylnitrosamine, phenylhydroxylamine, phenylsulphaminic acid, diacylanilides, the semidine and benzidine rearrangements, the change of diazoaminobenzene into aminoazobenzene, the catalytic change of alkylanilines into the ring-substituted isomers, the change of alkylpyridinium halides into α-alkylpyridines, the change of phenylpyrazoleiodomethylate into phenylmethylpyrazole, etc., etc., we see that Mr. Stieglitz is still playing the work of others in a "minor chord" in order to make a "major chord" of his own. His statement that he "overlooked" this work (p. 402) is *remarkable* in view of the fact that he admitted to me last September that this was a new principle. It is *impossible* that he could have "overlooked" the 35 and more pages bearing on this particular work in my April and September articles, which he has read[1] and cited, or "overlooked" the constant use on pp. 261, 303, 306, 339, 347 and 493 of this principle in my proof that the undissociated salts of amides, esters and cane sugar, etc., *are not* the particular substances chiefly *undergoing transformation.*

Another misrepresentation, against which I vigorously protest, is Mr. Stieglitz's discussion of my proof that in the oxime work the second and third laws of catalysis do not hold, and that there is a change in equilibrium. *How can this work*

[1] His *misrepresentation* of the facts *3 months later* proves his *guilt.*

be a copy of any of Stieglitz's work when he has done absolutely nothing on reversible reactions? He tries to hide my priority in these new ideas by exclaiming that (p. 411) any "investigator in the field could have told him that" and (p. 410) "no one ever claimed they should" hold, but we notice that he fails to give any references to show that he or any one else ever *thought* of the matter. The obvious fact is that no one ever presented the idea or discussed, before Abel, Euler and I took up the matter *for the first time*, whether they should or should not hold in such cases. And especially amusing and inconsistent is his long *tirade* to the effect that my work on the oximes violates the *old definitions of catalysis* because I have appreciable amounts of salts formed. Yet Mr. Stieglitz heads his papers "Catalysis of Imidoesters," and takes up the study of these imidoesters just because they do form well-defined salts! He *very carefully* "overlooks" the fact that, as a result of our work on catalysis, I have already (September, pp. 348–355; February, pp. 300–309) pointed out that the *old definitions* no longer hold, and that I have broadened them to include such new cases.

Stieglitz's comparison of the change of equilibrium in the oximes with the action of alkalies on a mixture of acid, alcohol, ester and water (*acids*, NOT ALKALIES, *bring about this reversible catalytic reaction!*) brands him as *guilty*[1] either of the grossest ignorance of the application of the mass law, or of deliberate misrepresentation of my work. In his example some of the organic acid is neutralized and absolutely removed from participation in the equilibrium, because the alkali salt formed could not possibly react with the alcohol and form an ester. Hence the apparent equilibrium between the *original* amount of acid, alcohol, water and ester would be disturbed, although the *real* equilibrium between the remaining substances would not. But in the oxime work the addition of more acid *increases* the reacting substances, no one of the reacting constituents is thrown out of the equilibrium reaction

[1] I challenge Mr. Stieglitz to give *even one* reference to prove his statement that (p. 411) "$CH_3C(ONa)(OH)(OR)$ is generally considered to be an intermediate product" in the hydrolysis of esters, amides, etc., by alkalies. I brought this out *the first time* in September and Mr. Stieglitz has "overlooked" this fact. I proved then (p. 344) that the *onions* of such salts decompose.

in the least, and yet the equilibrium is greatly changed by change in the concentration of the catalyzing acid for the reasons given in September[1] and February.[2] To illustrate with our simplest case, the same equilibrium point is obtained whether we start with acetoxime, water and one equivalent of acid, or with acetone, hydroxylamine and one equivalent of acid: the addition of more acid then changes the equilibrium point. The following scheme represents briefly the equilibrium, as far as we know at present, but the change of equilibrium is independent of the question whether the reaction is that of the cation or undissociated salt:

$$(CH_3)_2CO + \overset{+}{N}H_3OH + \overset{-}{Cl} \rightleftarrows$$

$$(CH_3)_2C{=}\overset{+}{N}HOH + \overset{-}{Cl} + H_2O \rightleftarrows$$

$$(CH_3)_2C{=}NOH + \overset{+}{H} + \overset{-}{Cl} + H_2O.$$

Our work and that of Lapworth[3] shows that when less than one equivalent of acid is used the equilibrium is still further changed, and that at least two other reactions set in.

Mr. Stieglitz showed very plainly in our correspondence of last summer that he intended to ignore me and the other workers in catalysis, and "read my new work into his 1904 paper." All that I cared to do in September and January was to point out that Stieglitz's ideas of 1904 were not new, were already public property, and that Stieglitz had used them without proper acknowledgment, whereas I gave all of my colleagues full credit for their ideas in September and January, and included Stieglitz's imidoester-cation hydrolysis. Through his use of Kastle's idea of the intermediate union of the catalyzing acid and the ester, amide, etc.; through his acknowledgment that Bredig's ideas (1903) of ester-cation and sugar-cation hydrolysis are correct; through the fact that Lapworth (1904) showed that ester and acid cations are hydrolyzed or alcoholized; to all of whom I gave *full credit*;[4] and especially through his mistakes in his St. Louis paper

[1] THIS JOURNAL, **38**, 309, 349, etc.

[2] *Ibid.*, **39**, 400.

[3] J. Chem. Soc., **93**, 85.

[4] That I did give *full credit* is shown, I believe, by the fact that in a recent article (Ber. d. chem. Ges., **41**, 755) Bredig speaks of the idea of *intermediate compounds* "das schon in vielfachen anderen Fällen bei der Katalyse angenommen und nachgewiesen wurde" and then says (footnote) "Literatur siehe bei Acree, l. c."

in the very mass law that he tried to use, Mr. Stieglitz's absurd claim in December that I got from him *my ideas, absolutely different from anything he has done*, not only falls, therefore, but in doing so brings him down in his guilt of having misrepresented me, of having tried to "appropriate" my new ideas, and of having presented his ideas without proper acknowledgment to others.

Once the idea of the formation of any kind of intermediate compound is given, as Kastle did in 1898, Acree in 1902, Bredig in 1903, Lapworth in 1904, etc., it becomes a question of experimental and mathematical detail to determine whether an undissociated salt,[1] a cation,[2] an anion[3] or a neutral molecule[4] is the substance undergoing transformation. I made it perfectly clear to my readers in my September article in my *General Discussion* (p. 297) and the discussion of reversible reactions (p. 334) that the above ideas had already been advanced by (pp. 299, 300, 301, 342) Bredig, Lapworth, Euler, Goldschmidt, Stieglitz, Acree, and then I gave Acree and Johnson's new work and new ideas (pp. 342–355).

Mr. Stieglitz knows only too well that his keynote is, as I pointed out in January, the same keynote that all the rest of us use. He knows only too well that in all physico-organic work, we all use the same mass law, which did not originate with Stieglitz; *that catalytic reactions are at bottom not different from any other reactions; that all the results depend upon the constants expressing the formation and reactions of the reacting constituents*; that this can be the only basis of quantitative experimental attack; and that every other chemist must therefore use the same principles.

[1] Acree and Johnson's rearrangement of acetylchloraminobenzene, and probably the analogous changes of phenylhydroxylamine, phenylnitramine, phenylsulphaminic acid, the semidine rearrangement, etc., etc.

[2] Bredig and Lapworth's ester, sugar, acid, etc., cations; Stieglitz's imidoester cations; Acree and Johnson's acetoxime and hydroxylamine cations; etc.

[3] Acree and Johnson's and Lapworth's work on hydroxylamine anions; Bredig's and Lapworth's work on complex benzaldehyde-cyanide anions, Bredig's catalysis of hydrogen peroxide by an iodoso anion; Acree's work on the action of urazole and other anions on alkyl halides; etc.

[4] Stieglitz and Upson's and Auwer's work on the rearrangement of aminophenylalkyl carbonates, and similar cases; Acree and Johnson's and Lapworth's work on the union of acetone and hydroxylamine.

Johnson and I showed experimentally *for the first time* that the question whether the second or third law holds varies widely with the different experimental problems. Stieglitz has, wilfully or otherwise, missed the point of our work on acetylchloraminobenzene, which was done to prove that even in this case of *pure catalysis*, in which the amount of salt is inappreciably small, the second law of catalysis does not hold. He has missed the whole point of our oxime work, wilfully or otherwise, which was done purely to prove that in the cases in which the salt formation is appreciably large, cases which do violate the old definition of catalysis, the second and third so-called laws do not hold, but yet the mechanism of the catalysis is the same as in some other cases. In other words, I feel with Euler, Abel, Bredig and Bodenstein, that *there is no sharp dividing line* between the cases of *pure catalysis*, in which the amount of intermediate compound formed is inappreciable, and those cases of *pseudo-catalysis* in which the concentration of the intermediate products is comparatively large and the catalyzer is used up in forming the end products. I pointed out in my September paper, on p. 349, in discussing the three so-called laws of catalysis, that "these laws are not laws at all but apply only to certain special cases," that "they cannot be used to make predictions concerning all catalytic reactions, but are only approximate expressions of special reactions," and that "there are two classes of reaction that must be considered in showing that these laws for catalysis by acids (or bases) do not hold," etc., etc. All of these ideas were made perfectly clear in my definition of a catalyzer on pp. 259, 348–355 and also in an article in THIS JOURNAL, **39**, 308.

I do not propose to spend any more time in correcting the mistakes and *deliberate misrepresentations* of Mr. Stieglitz.[1]

JOHNS HOPKINS UNIVERSITY,
March 12, 1908.

[1] I went to Chicago in 1905 primarily to assist two of my students, Mr. Stine and Mr. Holmes, in their organic preparations and to get Mr. Stine started on a dissertation. Prof. J. C. Hessler and Dr. Stine will corroborate me in the statement that I directed Dr. Stine in the study of the bromination of acylanilides. I went there, furthermore, to continue the researches on tautomerism which I was directing in Johns Hopkins University, and I took with me from Baltimore many of my urazoles, etc. Mr. Stieglitz had published some wrong ideas on tautomerism in his paper on indicators.

ON THE THEORY OF INDICATORS AND THE REACTIONS OF PHTHALEINS AND THEIR SALTS.

By S. F. Acree.

(We are being aided in our work on tautomerism by grants from the Carnegie Institution of Washington.)

I wish, as a preface to this article, to *lay especial emphasis* on the fact that, in answer to my statement[1] that he (Mr. Stieglitz) "had expressed 'wrong ideas' in an article on the theory of indicators"[2] Mr. Stieglitz *commits himself now in March, 1908*, as still believing his ideas of 1903 to be essentially correct. He does this by stating that "the (Acree's)[2] allegation was not true, the wrong ideas being wholly the creation of Mr. Acree's imagination."[3] The ideas in the following article, ideas partly mine, partly those of others, show that Mr. Stieglitz's wrong ideas were many more than those indicated in his sentence 'the wrong ideas' were that I (Stieglitz)[2] had overlooked the ionization and salt formation of the phenol groups in the phenolphthalein reactions."[2]

I lay emphasis on this point because Mr. Stieglitz tried in December to "appropriate" my new ideas in catalysis and misrepresented me in regard to a conversation of 1905, and I wish to forestall any chance for him to "discover" that any of the ideas in the following article were presented by him in 1903 or

and, when I arrived in Chicago, I invited Mr. Stieglitz to collaborate with me on tautomerism, each to furnish his own ideas and methods, just as Slimmer and Stieglitz had done (*vide* Slimmer and Stieglitz: This Journal, **31**, 661). Mr. Stieglitz told me that he was too busy to take up any further work. I do not wish it to be understood from my January article that I told Mr. Stieglitz any of my ideas on tautomeric salts or indicators, or pointed out to him his mistakes in his article on indicators. Naturally, when he told me that he could not join me, I did not care to discuss my ideas with him. I do not believe that we conversed 10 minutes at that time. I make this statement because Mr. Stieglitz misinterpreted, perhaps unconsciously, my sentence (p. 428): "While there I invited Mr. Stieglitz to collaborate with me (on tautomerism and *not* on catalysis) for our mutual benefit, as he had published a paper on tautomeric, compounds in which some wrong ideas were advanced." The clause "as he had published, etc." was intended by me to express *why* I thought of collaborating with Stieglitz, and is not to be interpreted as meaning that I pointed out his mistakes. Mr. Stieglitz has now stated that his wrong ideas are a "creation of Mr. Acree's imagination." I now leave it to my readers to determine whether my criticism of Mr. Stieglitz's views, found in the succeeding article, is just.

[1] This Journal, **37**, 72; **39**, 155.

[2] The words are mine for emphasis.

[3] Mr. Stieglitz's words: This Journal, **39**, 429.

in our conversation of September, 1907. Since I gave him this chance in *March, 1907*, to correct any former mistakes of which he was aware, and since he *commits himself* as being still of the opinion that there were no "wrong ideas" in his paper of 1903, I feel at liberty now to discuss the theories of indicators and dyestuffs from the point of view of the most recent contributions to this subject.

In Stieglitz's[1] article on "The Theories of Indicators" the most important new things are his equations, *which are certainly not entirely correct.*[2] By using the work of Bernsthsen, Nietzki and Schroeter, Nietzki and Burckhardt, Hantzsch and others on such tautomeric compounds, Stieglitz came to the conclusion, arrived at years before, that phenolphthalein behaves like a tautomeric compound, and that (p. 1115) "its red salts are the salts of a carboxylic acid, *not a phenol*,[3] and have the constitution

$$(MOOCC_6H_4)(HOC_6H_4)C:C_6H_4:O.$$

The strongly chromophoric quinoid complex ($:C_6H_4:O$) *gives us an explanation of the production of intense color, which is entirely adequate*[3] in view of the laws governing color in organic

[1] J. Am. Chem. Soc., **25**, 1112.

[2] An idea of considerable merit that Stieglitz has suggested in this indicator work is that of *quinhydrone formation* of which he spoke to me in September, 1907, and which he mentions now (THIS JOURNAL, **39**, p. 431, footnote), *and that is partly wrong*. Briefly, Stieglitz postulated to m ethat the alkali changes the phenolphthalein into the salt (see below) $(MeOOCC_6H_4)(HOC_6H_4)C:C_6H_4:O$. This, being both a quinone and a phenol, can form a phenoquinone (or quinhydrone) which would, in general, be more deeply colored than the quinone group and *hence be the chief source of colors in these indicators*. This idea, if correct, would account for the fact that the monophenol esters of phenolphthalein, etc., dissolve in alkalies with little color, the basis being that the quinone group and the phenol ester cannot form such colored quinhydrone derivatives (see Wichelhaus: Ber. d. chem. Ges., **12**, 1501; Hesse: Ann. Chem. (Liebig), **200**, 254). *One set of experiments shows that Stieglitz's idea is wrong.* If his idea were correct all aurine derivatives, having the group $C(C_6H_4OH)_2(:C_6H_4:O)$, and therefore forming this quinhydrone, would, by the addition of alkali, either not change in color at all or, if a diphenolate salt were formed, *the color would decrease. As a matter of fact the color increases* VERY GREATLY *exactly because the alkali salt* $—C(C_6H_4OK)(:C_6H_4:O)$ *is formed.* For all the evidence see the discussion below. I concur with Stieglitz in the belief that much of the color of the free aurines, etc. (*but not of their salts!*) is due to the kind of quinhydrone or phenoquinone formation spoken of by him, but I pointed out to him in September that I still was of the opinion that *my idea of tautomeric salts would explain both the color changes and the reactions of these salts.*

[3] Italics are mine for emphasis: see the discussion of these points below.

compounds." Then, on page 1122, he gives the equation $C_Q \times C_H = K'' \times C_{LH}$, and says (page 1122) "its tendency to produce the *red color* (*the red salt*[1]) is measured by the same constant K''."

Both of the above ideas, that of the constitution of the colored salts and the equation expressing the affinity constant of the phenolphthalein and its tendency to form the red salt *are wrong*. I wish to give here a short statement of our results and the ideas which we are using in this laboratory in studying this problem, which prove that the *quinone theory alone is not adequate, that the chief red salt is a phenol salt*, and that Stieglitz's equations and ideas concerning the formation, constitution and reactions of these salts are wrong. I do not discuss this subject here to impugn Stieglitz, who has at no time claimed that his views on tautomerism are to be considered seriously, but to present some ideas on which I have been gathering evidence during several years in my work on tautomerism. I do not claim any special credit for these ideas, as the facts which make them a necessary assumption to any one with an intimate knowledge of the dyestuffs have long been known. I shall discuss here only the acid tautomeric indicators, and these briefly. But the views hold, in the main, just as well for the basic tautomeric dyes and I shall discuss the entire matter later at more length. I should have brought out these ideas some time ago if I had had the quantitative proof of certain tautomeric phenomena.

I pointed out, however, in my first note that I believed that both of the phenol groups are acids, and that the idea of tautomeric salts would explain the color changes and reactions of phenolphthalein salts. As I felt protected by my first note on tautomerism,[2] and as this quantitative work is necessarily slow, and my collaborators, Brunel, Shadinger, Nirdlinger and especially Johnson, have only recently been able to bring the work to the desired certainty, I have desisted from putting forward any *uncertain* ideas lacking in quantitative evidence.

[1] The italics and words in parentheses are mine for emphasis.

[2] This Journal, **37**, 71.

We have shown in this laboratory, and others have added evidence, that the *chief source* of color in such compounds as the salts of aurine, phenolphthalein, etc., is not the quinone complex but the phenol salt of such a quinone compound, which I shall call a *quinonephenolate group*. This colored group may exist in two or more forms, (1) and (2) below, in equilibrium, and the inter- or intramolecular mechanical change from one to the other, or a corresponding movement of electrons, is very probably connected with the color changes. If Stieglitz had only done a little more reading, especially in Friedländer's paper,[1] and those of Nietzki, to which he referred, he would not have made such a mistake. It was at that time well known that solutions of such substances as aurine and rosolic acid,

$$(\overset{+}{H}O\overset{-}{C}_6H_4)_2C:C_6H_4:O + \overset{+}{K}O\overset{-}{H} \longrightarrow$$

$$(\overset{+}{H}O\overset{-}{C}_6H_4)(\overset{+}{K}O\overset{-}{C}_6H_4)C:C_6H_4:O \rightleftarrows$$

(1)

$$(HOC_6H_4)C:C_6H_4{-}\overset{-}{O}\overset{+}{K},$$

$$\begin{array}{c} | \quad | \\ C_6H_4O \end{array}$$

(2)

which already have the quinone complex, become *far*[2] more intensely colored when alkalies are added and the phenol salt is formed. Mr. E. A. Slagle finds that practically colorless solutions of aurine become a deep pink. Nietzki and Burckhardt, to whom Stieglitz referred, showed that the carboxyl ester of tetrabromphenolphthalein,[3]

$$(C_2H_5OOCC_6H_4)(HOC_6H_2Br_2)C:C_6H_2Br_2:O,$$

which already has the quinone complex, gives, in dilute, practically colorless solutions, a blue salt when the phenol group is neutralized by alkalies. But the isomeric phenol ethyl ester, which cannot form a quinonephenolate group, dissolves

[1] Ber. d. chem. Ges., **26**, 172.

[2] See Sutton's "Volumetric Analysis," 1901, p. 38, etc.

[3] Ber. d. chem. Ges., **30**, 177–178.

in alkalies without color.[1] Nietzki and Schroeter,[2] and Mr. Slagle and I, have shown that the fluoresceïn phenol ester, which cannot form the quinonephenolate complex, dissolves in alkalies with very little color, whereas fluoresceïn gives a deep color because it does form such a colored quinonephenolate complex. Likewise, Green and King,[3] and Mr. Slagle and I, have found that the carboxyl esters of phenolphthalein give the same intense color with alkalies that phenolphthalein itself does, because both can form the analogous colored salts,

$$(ROOCC_6H_4)(\overset{+}{K}\overset{-}{O}C_6H_4)C{:}\,C_6H_4{:}\,O$$

and

$$(\overset{+}{K}\overset{-}{O}OCC_6H_4)(\overset{+}{K}\overset{-}{O}C_6H_4)C{:}\,C_6H_4{:}\,O.$$

But the isomeric phenol methyl ester of phenolphthalein dissolves in alkalies practically without color because it cannot form such a quinonephenolate complex, but gives the salts

$$(\overset{+}{K}\overset{-}{O}OCC_6H_4)(CH_3OC_6H_4)C{:}\,C_6H_4{:}\,O \rightleftarrows (CH_3OC_6H_4)(\overset{+}{K}\overset{-}{O}C_6H_4)C{:}\,(OOCC_6H_4).$$

Phenolphthalein is useful as an indicator *only* because it forms, not the monobasic salt postulated by Stieglitz,

$$(\overset{+}{K}\overset{-}{O}OCC_6H_4)(HOC_6H_4)C{:}\,C_6H_4{:}\,O,$$

but the dibasic salt

$$(\overset{+}{K}\overset{-}{O}OCC_6H_4)(\overset{+}{K}\overset{-}{O}C_6H_4)C{:}\,C_6H_4{:}\,O.$$

Meyer and Spengler,[4] who were the first to prove experimentally that the colored salts are dibasic salts, were inclined to give these salts the lactoid form. As early as 1893 Friedländer[5] pointed out that the relation of aurine to phenolphthalein leads to the conclusion that the red salts of phenol-

[1] Ber. d. chem. Ges., **30**, 178.
[2] *Ibid.*, **28**, 48.
[3] *Ibid.*, **40**, 3724.
[4] *Ibid.*, **38**, 1318.
[5] *Ibid.*, **26**, 172.

phthalein must be dibasic salts with the quinone nucleus. The carboxyl ester of phenolphthalein is a better[1] indicator than phenolphthalein itself because it takes only half as much alkali to form the really chromophoric group

$$RC(C_6H_4\overset{-}{O}\overset{+}{K})(:C_6H_4:O).$$

These ideas account for the fact that Bistrzycki's[2] diphenylquinonemethane,

$$(C_6H_5)_2C:C_6H_4:O,$$

is far less deeply colored than the salts of benzaurine,

$$C_6H_5C(:C_6H_4:O)(C_6H_4\overset{-}{O}\overset{+}{Na}),$$

and aurine,

$$(HOC_6H_4)(\overset{+}{Na}\overset{-}{O}C_6H_4)C:C_6H_4:O.$$

The latter can form the deeply colored quinonephenolate addition product, while the diphenylquinonemethane has no such group. The above ideas and space interference probably explain in part the lack of intense color in the salts of the various dioxy- and diaminotriphenylcarbinols and the corresponding trisubstituted compounds not having the substituent groups in the para positions. Examples of this class could be multiplied.

There is no longer any question that alkalies (acids) tend to cause the quinone group in all such compounds to become hydrated and colorless,[3] perhaps on account of salt formation. This accounts for the fading of the color when phenolphthalein, etc., are treated with an excess of alkali. Green and Perkin showed that the hydrate,

$$(HOC_6H_4)_2C(OH)C_6H_4COONa,$$

loses water only very slowly at lower temperatures.

The constitution of the colored compounds or the cause of the color are still to be cleared up, and it is immaterial for this hypothesis whether the views of Jackson or those of

[1] Ber. d. chem. Ges., **40**, 3728.

[2] *Ibid.*, **36**, 2337.

[3] Bistrzycki: *Loc. cit.*; Ber. d. chem. Ges., **36**, 3558, 3565. Green and Perkin: J. Chem. Soc., **85**, 398.

Posner[1] are correct. It suffices to say that the idea of the union of the metallic phenolate with the quinone complex, involving perhaps ionization, seems to be the central cause. Evidence for this lies in the fact that Jackson and Oenslager,[2] and also Wichelhaus,[3] have isolated deeply colored salts,

$$C_6H_4(ONa)_2(OC_6H_5)_2, \quad C_6H_4(ONa)_2(\beta\text{-}OC_{10}H_7)_2,$$

etc., which are formed by the union of sodium phenolate, or naphtholate, with quinone, and that Mr. Slagle and I have formed deeply colored compounds by the union of benzoquinone or anthraquinone with salts of *o*-cresol, *p*-cresol, phenol, hydroquinone, pyrogallol and resorcinol, the color of which disappears when acids are added. In fact such mixtures serve as very good indicators.

We suspect, further, that alkaline solutions of pyrogallol, etc., become colored when oxidized merely because some of the pyrogallol gives a quinone which then forms a quinone-phenolate with some of the unchanged alkali salt of the pyrogallol, etc., or with the salt of some of the products of oxidation. When acids are added the color fades just as in the experiments spoken of above.

Exactly the same kind of reasoning applies to the color changes in rosaniline and similar compounds, only in this case the chief colored substance is formed by the union of the quinone group (itself a salt) and a free base, instead of a quinone and salt, as in the aurine and phenolphthalein groups. In the rosaniline series the colorless carbinol, a very weak base, is in equilibrium with a trace of the quinone complex, a much stronger base:

$$\left.\begin{array}{ccc} (NH_2C_6H_4)_3COH & \rightleftarrows & (NH_2C_6H_4)_2C{:}C_6H_4{:}NH_2OH \\ \uparrow\downarrow & & \uparrow\downarrow \\ (NH_2C_6H_4)_3\overset{+}{C} + \overset{-}{OH} & & (NH_2C_6H_4)_2C{:}C_6H_4{:}\overset{+}{N}H_2 + \overset{-}{OH} \end{array}\right\} \rightleftarrows$$

$$(NH_2C_6H_4)_2C{:}C_6H_4{:}\overset{+}{N}H_2\overset{-}{O}H.$$

[1] Ann. Chem. (Liebig), **336**, 85.
[2] THIS JOURNAL, **18**, 1.
[3] Ber. d. chem. Ges., **8**, 849.

When an equivalent of a stronger acid is added, much salt,

$$(NH_2C_6H_4)_2C:C_6H_4:\overset{+}{N}H_2\overset{-}{Cl},$$

of the stronger base is formed, and incidentally there is a deep color produced. *Now the* CHIEF CAUSE *of this color is not the colored quinone group, as Mr. Stieglitz believed, but the double compound formed by the inter- or intramolecular union of the quinone complex with the free aniline (or aniline hydroxide) groups of the dyestuff.* One of the possible modes of union is shown by the dotted lines in the above equation. In order to show the analogy of these colored compounds to the quinhydrones and phenoquinones we shall call them *quinaminones.* What is the evidence?

Jackson and Clarke[1] showed very clearly that in non-aqueous solutions *o*- and *p*-quinones form deeply colored addition products with aromatic amines, but not with the amine salts. They isolated, for example, the unstable compounds,

$$C_6Br_4O_2.C_6H_5N(CH_3)_2, \quad C_6Cl_4O_2.C_6H_5N(CH_3)_2,$$

etc., which were formed by the *reversible* union of one molecule of dimethylaniline with one molecule each of tetrabromorthoquinone, chloranil, etc. Mr. Slagle and I have been able to show that the same phenomena are exhibited beautifully in aqueous solutions. The addition of an equivalent amount of an aqueous solution of dimethylaniline hydrochloride to one of quinone produces no color change; but when an alkali is added to the solution and the dimethylaniline is liberated, the quinone and amine unite to some extent in a reversible reaction, and the color changes to a brownish red or brownish purple: the addition of an acid removes the amine and hence causes the color to fade to that of the quinone. The addition of an aqueous solution of a salt of α-dimethylamino-α-bromnaphthalene to one of quinone produces no color change. But when an alkali is added gradually and the amine base is liberated, the quinone and amine unite to some extent and form some *quinaminone*, and the color changes

[1] THIS JOURNAL, 34, 441.

successively to yellow, pink and a deep brown. When the solution is acidified and the amine is neutralized the color fades to that of the quinone.

These experiments prove conclusively that quinones form addition products with anilines and naphthylamines (but not with their salts) which are far more deeply colored than the quinones themselves.

The reactions of all the dyestuffs analogous to the rosaniline series prove the same point. Evidence for this *quinaminone* formation is found in a large number of facts similar to the following: *p*-Aminotriphenylcarbinol and acids give only an orange color from the quinone group of the salt

$$(C_6H_5)_2C:C_6H_4:\overset{+}{N}H_2\overset{-}{Cl}.$$

But the *p,p*-diaminotriphenylcarbinol gives an intense violet color because it forms, to some extent, the deeply colored *quinaminone* group in the salt

$$(NH_2C_6H_4)(C_6H_5)C:C_6H_4:\overset{+}{N}H_2\overset{-}{Cl}.$$

Now if the color is due chiefly to the *quinaminone* group instead of the quinone group, the addition of more and more acid should cause a *decrease* in the color because the amine groups would be converted into their salts, which do not unite with the quinone group and form the colored *quinaminone*. The evidence certainly sustains the above hypothesis. The addition of hydrochloric acid to malachite green causes a fading of the color, as the amino group is neutralized, from bluish green to greenish yellow and then to reddish yellow, which is probably the modified color of the quinone group. The addition of alkali causes a reversal of these color changes to the original bluish green, because the quinaminone group is then reformed from the liberated amino group and the quinone. An excess of alkali, of course, converts the salt into the base which then rearranges into the colorless carbinol. The addition of hydrochloric acid to a fuchsine solution causes a change from the intense carmine red to a much less intense

reddish yellow, which is probably the color of the quinone group modified by the various auxochromes. When the acid is neutralized the original color is restored. Examples could be multiplied.

The point is that the CHIEF SOURCE *of color in indicators (both basic and acid) and substances of these types is not the quinone group, but one or more*[1] *inter- or intramolecular combinations of a quinone group with a salt of phenol, or with an anilinelike group. A small amount of color is, of course, due to the quinone group because all quinones are somewhat colored.*

I am not alone in differing from some of the views presented by Stieglitz, as Baeyer has recently pointed out some of the above relations in a valuable article[2] on the dyestuffs and Hantzsch has suggested similar ideas to account for the color of his nitrophenol salts, while King and Green think that the colored salts of phthaleins may be hydrated. Baeyer tested the above hypothesis, advanced first by Jackson, by trying to obtain colored solutions by the use of fuchson, or fuchsonimonium chloride, and sodium phenolate, or dimethyl-*p*-toluidine. No colors were obtained and he discarded the quinonephenolate hypothesis in favor of ideas similar to those used by Hartley and by Baly.[3] Our experiments with quinones and phenolates and aromatic amines, however, gave beautiful color reactions, a result not easily explained by the ideas of Hartley and Baly, as applied by Baeyer. As I see it, all of the facts known at present are readily understood when Jackson's ideas and the oscillation hypothesis of Baly are used, and I have given them preference above. We must keep our minds open to the fact that both, and perhaps other explanations, may be concerned in these complicated phenomena, and this communication is to be considered only in that light.

In our quantitative study of these phenomena we shall try to determine all of the quantitative relations between

[1] Several possibilities present themselves, and these may be the source of the different colors shown in the absorption spectra of these dyestuffs, and exhibited by their solutions under varying conditions of dilution, acidity, alkalinity, temperature, etc.

[2] Ann. Chem. (Liebig), **354**, 162.

[3] J. Chem. Soc., **85**, 1029; **89**, 502, 514; **91**, 426, 1572.

the color intensity and all of the equilibrium and dissociation constants. We shall study the relation between the concentration of the sodium phenoquinonate and of the quinone and the sodium phenolate and its ions,

$$(1 \text{ or } 2)C_6H_5O,\overset{-}{\underset{}{}}\overset{+}{Na} + O:C_6H_4:O \rightleftarrows O:C_6H_4:O(1 \text{ or } 2)C_6H_5O,\overset{-}{\underset{}{}}\overset{+}{Na},$$

and the relation between the concentration of the *quinaminone* and of the quinone and aniline derivatives, etc.:

$$C_6H_5N(CH_3)_2 + O:C_6H_4:O \rightleftarrows O:C_6H_4:O.C_6H_5N(CH_3)_2.$$

We shall study especially the possible relation between the color intensity and the dissociation constants of the phenol salts and quinone salts. This will be done in the simple cases as well as with the tautomeric phthaleins, rosanilines, etc.

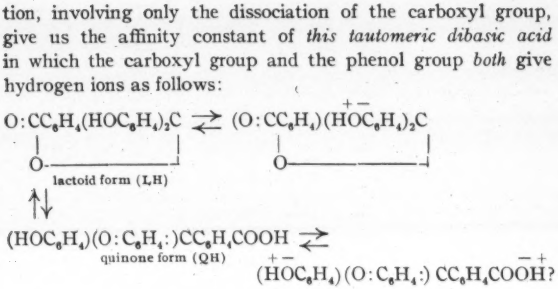
It is needless to say, as I pointed out in a former paper,[1] that "there is not sufficient quantitative evidence on hand to enable us to see clearly the mechanism of the reactions involved in the changes from the colorless to the colored substances, or *vice versa*, or to say whether the changes are molecular or ionic, whether they take place directly or through intermediate stages. The ionic theory and the chromophoric theory have such a hold upon us that we attempt to interpret all of the above changes by means of them. They may contain a great deal of truth, but also a great deal that must ultimately be discarded. What we need is a large amount of quantitative work to help us find the truth." For this reason I wish to state that the ideas on tautomerism discussed in the succeeding pages, as well as those in the preceding sections, are based on the results of our rigorous qualitative and quantitative work in the field of tautomerism, and especially with the urazoles.

And now we come to that equation $C_Q \times C_H = K'' \times C_{LH}$ which Stieglitz said gives us the affinity constant of a tautomeric compound like phenolphthalein, or the tendency to produce the red color or red salt.[2] How can any such equa-

[1] This Journal, **38**, 28.

[2] For his development of this equation and the terms used see J. Am. Chem. Soc., **25**, page 1122.

tion, involving only the dissociation of the carboxyl group, give us the affinity constant of *this tautomeric dibasic acid* in which the carboxyl group and the phenol group *both* give hydrogen ions as follows:



How can any such equation, *expressing only the dissociation of the carboxyl group*, give us the "tendency to form the red color" from the red salt when that red salt is the dibasic *carboxyl* and *phenol* salt? It is perfectly evident that *a formula giving the correct affinity constant must take into consideration the two different tautomeric forms and the extra phenol group*, and a reference to a paper by Acree in THIS JOURNAL, **38**, 1, will show Mr. Stieglitz a large number of such cases worked out. *The ideas discussed in the succeeding pages, as well as those in the preceding pages, are the results of our rigorous experimental work in the field of tautomerism.*

It is further evident that the lactoid and quinoid forms are *weak*[1] dibasic acids and should be called LH_2 and QH_2 since each has two hydrogen atoms replaceable by metals. The carboxyl group of QH_2 is without doubt stronger than the phenol group. The development of the affinity constant of the phenolphthalein must be directly related to the affinity constants K_1 and K'_1 of the lactoid form LH_2, to the affinity constants K_2 and K'_2 of the quinone form QH_2, and to K_3, the equilibrium constant of the two tautomeric forms. I assume that the molecular forms of these acids and salts are in equilibrium because Dimroth[2] and Acree[3] have proved such to be the case with other tautomeric acids and salts

[1] McCoy: THIS JOURNAL, **31**, 503. Salm: Z. physik. Chem., **57**, 471. Veley: *Ibid.*, **57**, 147; **61**, 464. J. Chem. Soc., **91**, 156.

[2] Ann. Chem. (Liebig), **335**, 1; **338**, 143.

[3] THIS JOURNAL, **37**, 71; **38**, 1.

and I reserve the right to use our other form of equation when we prove in any case that the anions or cations are in equilibrium.

Now Ostwald,[1] Smith,[2] Noyes[3] and Trevor[4] have shown that such weak dibasic acids obey Ostwald's dilution law. We therefore have

$$C_{LH} \times C_H = K_1 C_{LH_2}, C_{QH} \times C_H = K_2 C_{QH_2}, \text{ and } C_{LH_2} = K_3 C_{QH_2}.$$

From this it follows that the affinity constant of the phenolphthalein is represented as accurately as our present experimental methods will show by the equation

$$\frac{(C_{LH} + C_{QH}) \times C_H}{(C_{LH_2} + C_{QH_2})} = \frac{K_2 + K_1 K_3}{1 + K_3} = K,$$

which is quite different from Mr. Stieglitz's equation,

$$C_Q \times C_H = K'' \times C_{LH}.$$

That my equations are the correct ones for showing the affinity constants of such weak tautomeric acids was not only developed theoretically by the use of the mass law, but proved experimentally by Acree and Shadinger[5] in the work on a large number of tautomeric urazoles. The equation

$$\frac{H \times (C_{hi} + C'_{hi}, \text{ etc.}, + C_{ei} + C'_{ei}, \text{ etc.})}{(C_h + C'_h, \text{ etc.}, + C_e + C'_e, \text{ etc.})} = K,$$

for instance, was shown to hold perfectly well for substances (phenylurazole, etc.) having a large number (four or more) of weakly tautomeric acid forms.

But the tendency to form the red salt or red color is still more complicated than Mr. Stieglitz thought. The moment LHNa and QHNa are formed, they set up, as our work on tautomerism shows, their own equilibrium conditions practically instantaneously, as follows:

[1] Z. physik. Chem., **3**, 280.
[2] *Ibid.*, **25**, 144, 193.
[3] *Ibid.*, **11**, 495; **13**, 417.
[4] *Ibid.*, **10**, 321.
[5] THIS JOURNAL, **39**, 124. Shadinger: Dissertation, Johns Hopkins Univ., 1907.

$$(O:C_6H_4:)(HOC_6H_4)CC_6H_4COONa \underset{K'_3}{\rightleftarrows}$$
(1)

$$(HOC_6H_4)(NaOC_6H_4)C:(OCOC_6H_4) \underset{K''_3}{\rightleftarrows}$$
(2)

$$(NaOC_6H_4)(O:C_6H_4:)CC_6H_4COOH.$$
(3) (a trace)

Of the three monoalkali salts (1) and (3) give some color but even that is faint in comparison with the color of their corresponding dimetallic salt, QNa_2. (1) and (3) yield directly the colored salt,

$$(\overset{+}{\text{Na}}\overset{-}{\text{O}}C_6H_4)(O:C_6H_4:)CC_6H_4\overset{-}{\text{C}}O\overset{+}{\text{O}}Na,$$

and (2) yields this colored salt *indirectly* through the tautomeric rearrangement of the dimetallic salt, LNa_2, corresponding to (2).

If we call C_{QHNa} the concentration of (1), C_{LHNa} that of (2), and C_{QNaH} that of (3), and consider that (1) dissociates partly into H and C_{QNa}, while (3) gives H and C'_{QNa}, and recognize the possible ionization of all these, the affinity constant of this tautomeric monosodium salt must be expressed approximately by a complicated equation having *something* of this form, though not exactly,

$$\frac{C_H \times (\bar{C}_{QNa} + \bar{\bar{C}}_Q + \bar{C}_{LNa} + \bar{\bar{C}}_L + \bar{C}'_{QNa}, \text{ etc.})}{(C_{QHNa} + C_{LHNa} + C_{QNaH}, \text{ etc.})} = K,$$

in which K is a very complex function involving the dissociation constants of these acid salts and the equilibrium constants K'_3 and K''_3.

For the total amount of the disodium salt formed the following equilibrium relations would hold for the undissociated portions:

$$(NaOC_6H_4)_2C:(OCOC_6H_4) \rightleftarrows$$
(4)

$$(NaOC_6H_4)(O:C_6H_4:)CC_6H_4COONa \underset{K'''_3}{\rightleftarrows}$$
(5)

$$(NaOC_6H_4)(O:C_6H_4:)CC_6H_4COONa,$$
(6)

in which K'''_3 is intended merely to express the probable equilibrium between the actual deeply colored salts (6), whatever their nature, and the quinone dibasic salt (5). It is evident then that the color of the phenolphthalein solution is due to some extent to the salts (1), (3) and (5), but *chiefly* to (6), which may exist in several forms. We are investigating the decrease of the color of these salts in alcohols, acetone, etc., from the following points of view: (1) that in these solvents a change of the equilibrium results and much more of the salt (4) is formed; (2) that the quinone group takes up alcohol readily and becomes colorless; and (3) that the salts (4), (5) and (6) are changed in dissociation. When we learn the values of all the above constants we can easily express in numbers the affinity constant of phenolphthalein and its "tendency to give the red color."

The above ideas lead to equations which express the *sensitiveness* of indicators to acids and alkalies, already discussed by Ostwald. These equations are developed in the way already published[1] and will be given in detail in our full report.

Stieglitz's equation above not only fails to give the affinity constant of phenolphthalein, *but does not even show the tendency of the phenolphthalein to give the red salt or the red color.* It fails to do so purely because it gives an approximation of the tendeney to form a salt

$$(\overset{+}{M}OOCC_6H_4)(HOC_6H_4)C:C_6H_4:O,$$

which is not the colored salt or salts,

$$(\overset{+}{M}OOCC_6H_4)(\overset{+}{M}\overset{-}{O}C_6H_5)C:C_6H_4:O),$$

chiefly concerned.

Not only do the above ideas of tautomeric acids and salts lead us to a clearer understanding of the color changes involved in phenolphthalein, fluoresceïn, etc., but they also make clear the formation of the various esters when the salts of such compounds are treated with alkyl halides. Potas-

[1] THIS JOURNAL, 38, 1.

sium fluoresceïn and ethyl iodide give the four possible mono- and diethyl esters.[1] Our ideas on such tautomeric salts have been proved *quantitatively*[2] by our work on urazoles and are being extended in several directions. The following formulae will show the outline of the work that we are carrying forward, the validity of which will be tested by quantitative methods. We believe that such formulae represent, at least to a large extent, the constitution of the salts, whose undissociated forms are the ones probably in equilibrium, which in solutions are ionized, which give us the color, and the anions of which yield the esters. We use phenolphthalein merely as an example.

Monobasic salts:

$$(O:C_6H_4:)(\overset{+}{H}OC_6H_4)CC_6H_4COO\overset{-}{K} \rightleftarrows$$

(somewhat colored)

$$(HOC_6H_4)(\overset{+}{K}OC_6H_4)C(OCOC_6H_4) \rightleftarrows$$

(colorless)

$$(\overset{+}{K}OC_6H_4)(O:C_6H_4:)CC_6H_4COOH.$$

(deeply colored)

Dibasic salts:

$$(\overset{+}{K}OC_6H_4)_2C\begin{array}{l}-C_6H_4\\ \quad|\quad\ |\\ \quad O-CO\end{array} \rightleftarrows (\overset{+}{K}OC_6H_4)(O:C_6H_4:)C-C_6H_4COOK$$

(colorless) (deeply colored)

$$(\overset{+}{K}OC_6H_4)_2C(OH)C_6H_4COOK.$$

(colorless)

The anions of these tautomeric salts seem to react with the alkyl halides and yield the various tautomeric esters in the manner proved quantitatively for the urazoles.[3] In certain cases some of the esters may rearrange into others,

[1] Ber. d. chem. Ges., **28**, 48.

[2] Acree: This Journal **37**, 71. Acree and Shadinger: *Ibid.*, **39**, 124. Shadinger: Dissertation, Johns Hopkins Univ., 1907. Acree, Brunel, Shadinger, Nirdlinger and Johnson: Article on tautomeric salts read before the Am. Chem. Soc., Jan. 1, 1908.

[3] Brunel: Dissertation, Johns Hopkins Univ., 1906. Acree: This Journal, **37**, 71; **38**, 1. Acree and Shadinger: *Ibid.*, **39**, 226. Acree: Year Book of the Carnegie Institution of Washington, No. 6, p. 178. Acree, Johnson, Brunel, Shadinger and Nirdlinger: An article on tautomerism] soon to appear in This Journal.

as Meyer[1] has recently found, and as has been shown in the isomeric change of the O-esters of urazoles, oxylepidine, quinazolines, amides, etc., into the corresponding N-esters. We are investigating the reactions of phenolphthalein, fluorescein, etc., with alkyl halides, diazomethane, -ethane, etc.

JOHNS HOPKINS UNIVERSITY,
February 20, 1908.

STUDIES IN BROMINATION: A REPLY TO COHEN AND CROSS.[2]

BY S. F. ACREE, J. M. JOHNSON AND SIDNEY NIRDLINGER.

In answer to the statement of Cohen and Cross that part of our ideas[3] that such compounds as

$$CH_3CONHBr_2C_6H_5$$

are intermediate substances in the formation of the compound

$$CH_3CONBrC_6H_5,$$

etc., and in its catalysis by hydrobromic acid were derived from their work, we wish to point out the following:

(1) Mr. Nirdlinger's notebook[4] shows that his compound,

$$CH_3CON(CH_3)Br_2C_6H_5,$$

analogous to the compound,

$$CH_3CONHBr_2C_6H_4CH_3,$$

of Cohen and Cross, was analyzed on March 9th, 1907, or two months before Cohen and Cross published their paper. We should have mentioned this in April,[5] September[6] and December if we had anticipated any controversy.

(2) On page 272 of our September paper and 747 of our December paper we gave Jackson and Clarke[7] credit for priority in the experimental proof of the idea used by us

[1] Meyer and Marx: Ber. d. Chem. Ges., **40**, 1437.

[2] THIS JOURNAL, **39**, 431.

[3] *Ibid.*, **38**, 746.

[4] I have examined the notebook here referred to and I certify that the statement is in accordance with the fact.—EDITOR.

[5] THIS JOURNAL, **37**, 410.

[6] *Ibid.*, **38**, 265.

[7] *Ibid.*, **34**, 261; **36**, 409. Fries: Ann. Chem. (Liebig), **346**, 128.

that such a dibrom derivative is an intermediate compound in the strictly analogous reaction:

$$(CH_3)_2NC_6H_5 + Br_2 \rightleftarrows (CH_3)_2NBr_2C_6H_5 \longrightarrow$$
$$(CH_3)_2NHBrC_6H_4Br \rightleftarrows (CH_3)_2NC_6H_4Br + HBr.$$

We take pleasure too in stating that Professor K. J. P. Orton has called our attention to the fact that he has advocated this view for some years; his results are to be found in a number of interesting papers[1] on this and related rearrangements.

(3) The equation (1) which Cohen and Cross claim that we wrote in December for the first time is exactly like (2) which is found on page 273 of the September article, Cl simply taking the place of H:

(1) $CH_3CONHC_6H_5 + Br_2 \rightleftarrows CH_3CONHBr_2C_6H_5 \longrightarrow$
$CH_3CONHC_6H_4Br + HBr;$

(2) $CH_3CONClC_6H_5 + Br_2 \rightleftarrows CH_3CONClBr_2C_6H_5 \longrightarrow$
$CH_3CONHC_6H_4Br + ClBr.$

We do not lay any stress on this, the idea having already been advanced by Jackson and Clarke, and perhaps by others. Our interest in the matter lies chiefly in the quantitative side and in the light that we were able to throw on catalysis.

(4) The equations given by Cohen and Cross[2] are not in harmony with our results:

$$CH_3CONHC_7H_7 \longrightarrow \underset{\text{A.}}{CH_3CONHBr_2C_7H_7} \longrightarrow$$
$$\underset{\text{B.}}{CH_3CONBrC_7H_7} \longrightarrow \underset{\text{C.}}{CH_3CONHC_7H_6Br}.$$

The substance A., not B., is transformed directly into C., as was suggested by Orton, and definitely proved by the work of Jackson and Clarke and by our quantitative investigations.

Our December note was written in no controversial spirit, as we simply wished to point out that we have been engaged intermittently on this problem four years, and especially during the last two years. We are glad to welcome the inter-

[1] J. Chem. Soc., **83**, 796; **87**, 389; **91**, 146, 1543, 1554; and earlier papers.
[2] Chem. News, **95**, 274. Acree, Johnson and Nirdlinger: THIS JOURNAL, **38**, 747.

esting results of Cohen and Cross, or of any others, in this line of work. We have noticed some apparently abnormal rearrangements in this class of compounds which we shall continue to study.

JOHNS HOPKINS UNIVERSITY,
March 6, 1908.

REPORTS.

THEORIES OF OSMOTIC PRESSURE.

The Thermodynamic View.

The striking analogies between the osmotic pressure of solutions of cane sugar in water and the elastic pressure of gases, brought out by Pfeffer's work,[1] led van't Hoff to conclude that there is a deep-seated relation between the two sets of phenomena and he accordingly put forward his kinetic theory of solutions,[2] in which the osmotic pressure of dilute solutions is ascribed wholly to the bombardment of the membrane separating solution and solvent by the dissolved molecules, while in the case of more concentrated solutions the mutual attractions of solute and solvent come into play.[3]

He then attacked the problem from the theoretical side. Assuming a perfectly semipermeable membrane, he proved that the osmotic pressure of a dilute solution of a gas is equal in value to the elastic pressure which the solute would exert in the gaseous condition at the same temperature and volume. The solution must be so dilute that the mutual attractions of the dissolved molecules, as also the space actually occupied by them, are negligible. The method of proof is based on the assumption of a thermodynamically passive membrane, that is, one that permits the carrying out of a reversible cycle, and on the application of the second law of thermodynamics. Van't Hoff next passes from solutions of gases to solutions in general and concludes that for "ideal solutions," that is, solutions dilute enough to conform to the conditions named above, the laws of gases must hold.

In the development of the kinetic theory of gases, in its simplest form, the same assumptions with regard to concentration are made as were made by van't Hoff for solutions.

[1] Osmotische Untersuchungen, Leipzig, 1877.
[2] Z. physik. Chem., 1, 481 (1887).
[3] Address before the British Association at Leeds in 1890.

It is further necessary to assume that the gas molecules move with considerable velocities. The difficulties involved in making these assumptions when we come to deal with solutions have been repeatedly pointed out. Plainly, the case here is much more complicated. In solutions, besides the relatively small number of solute molecules, we have present an enormous number of molecules of solvent, so that even if we could neglect the mutual attraction between solute molecules, that between solute and solvent should probably be taken into account. It is to be noted, however, that the solute molecule is always *completely* surrounded by solvent molecules and hence the resultant of all the forces acting upon it, due to solvent, is zero, and consequently its velocity as it approaches the membrane is not affected, provided the solution is so dilute that we may neglect the difference in concentration of solvent molecules on the two sides of the membrane.

A further difficulty in the way of extension of the kinetic theory to solutions arises from the relatively slow rate of diffusion in liquids as compared with that of gases. With regard to this objection, it has been pointed out that what we are concerned with is not the velocity of diffusion in the ordinary sense. Diffusion velocity is determined by noting the time required by a molecule, for example, to travel through a finite distance, say from A to B, but during this interval the molecule has probably traversed many times this distance, by a zigzag path, experiencing a very large number of encounters with neighboring molecules, both of solute and solvent—a much larger number, probably, than the gas molecule meets with. The straight-line distance A B bears no known relation to the actual velocity of the molecule between successive impacts, and this velocity, which determines the kinetic energy of the particle and with which alone we are concerned, may be comparable with the velocity of the gas molecule.

As indicated above, van't Hoff's deductions were specifically limited to very dilute solutions. This is not surprising, inasmuch as the relation $PV = RT$ holds rigidly for gases only under the very conditions laid down by van't Hoff for solutions. For more concentrated gases van der Waals found it necessary to introduce correction terms for the mutual attractions of the molecules and for the space occupied by them. His equation has the form $\left(P + \frac{a}{V^2}\right)(V-b) = RT$. By their recent work, Morse and

Frazer and their coworkers[1] have greatly extended the range over which the gas laws apparently hold by regarding V in the equation $PV = RT$ as the volume of the *solvent* and not of the *solution*. This is in effect what van der Waals has done for gases, *viz.*, correcting for the space occupied by the molecules of the dissolved substance.

Lord Rayleigh,[2] by an independent though somewhat similar method of thermodynamic reasoning, arrived at the same conclusion formerly reached by van't Hoff as to the numerical identity between theoretical gas and osmotic pressures.

Prof. Larmor,[3] considering the subject in its relation to the general molecular theory, also places osmotic theory on the thermodynamic basis. His treatment is free from the objection urged by Lord Kelvin[4] to the method employed by van't Hoff and Rayleigh. Both these authors base their proofs upon the law of Henry, and Lord Kelvin seems to regard any extension of the theory to cases in which this law does not hold or in which there is a change in molecular aggregation on solution as unwarranted. Prof. Larmor, however, places the theory of osmotic pressure on a purely abstract basis. The laws of solubility of gases or possible change in the state of molecular aggregation during solution are not involved. To quote from him: "The following position is, I think, sound. Each molecule of the dissolved substance forms for itself a *nidus* in the solvent; that is, it sensibly influences the molecules around it up to a certain minute distance so as to form a loosely connected complex in the sense, not of chemical union, but of physical influence. The laws of this mutual molecular influence are unknown, possibly unknowable; but, provided the solution is so dilute that each such complex is for very much the greater part of the time out of range of the influence of the other complexes (as, for instance, are the separate molecules of a free gas), then the principles of thermodynamics necessitate the osmotic laws."

The experiments of Prof. William Ramsay[5] on the passage of hydrogen through a palladium septum, illustrating what has been termed the osmotic pressure of gases, are interesting as emphasizing the analogy between gas pressure and osmotic pressure. If a palladium vessel, heated to 250°–350°,

[1] This Journal, **34**, 1 (1905); **36**, 39 (1906); **37**, 324, 425 and 558 (1907).
[2] Nature, **55**, 253 (1897).
[3] Phil. Trans., **190**, 266 (1897); Nature, **55**, 545 (1897).
[4] Nature, **55**, 272 (1897).
[5] Phil. Mag. [5], **38**, 206 (1894).

is filled with nitrogen or some other gas not absorbed by palladium, say at atmospheric pressure, and the vessel immersed in hydrogen at a given pressure, the hydrogen will diffuse through the metal membrane till the increase of pressure inside the vessel is nearly equal to the pressure on the outside. For example, in one experiment in which nitrogen was used and the palladium heated to 280°, the two gases being at atmospheric pressure, the excess on the inside was 733 millimeters of mercury and the barometric height was 748.1 millimeters. This may be regarded as the osmotic pressure of nitrogen dissolved in hydrogen.

The author interprets his results as being in harmony with the view that osmotic pressure is to be ascribed to the dissolved substance, "though apparently caused by entrance of solvent." Whatever interpretation may be given to these observations as bearing on osmotic phenomena of solutions, Lowry[1] directs attention to the fact that here we have a case of a pressure, which is an almost exact analogue of osmotic pressure in liquids, actually produced by the bombardment of the walls of the vessel by nitrogen molecules, and this pressure is independent of the concentration of the hydrogen, inasmuch as the pressure due to hydrogen is the same on the two sides of the septum.

The Surface-Tension Theory.

B. Moore[2] in 1894 put forward the view of surface tension as a possible explanation of osmotic phenomena. Assume two liquids, A and B, of surface tensions T_1 and T_2, respectively, in vessels connected by a capillary tube of radius r, the liquids meeting in the capillary. Then the skin of liquid forming the surface of contact with the wall of the tube will be urged in the direction of A, if T_1 is greater than T_2, by a force $(T_1 - T_2)2\pi r$. If the radius of the tube is sufficiently small, that is, small enough to bring all the liquid in it within the range of capillary action, as is probably the case with ordinary osmotic membranes, the whole body of liquid in the capillary will be urged in the direction of A. Thus osmosis should proceed in the direction indicated, from the region of less to that of greater surface tension. He states four laws which might be expected to follow: (1) The surface tensions of all solutions obeying the other solution laws should be higher than those of the solvents. (2) For solutions of the same substance in the same solvent, surface tensions should be proportional to the concentra-

[1] Trans. Faraday Soc., 3, 12 (1907).

[2] Phil. Mag. [5], 38, 279 (1894).

tion. (3) For solutions of equal concentration of different substances in the same solvent the differences in surface tension between solution and solvent should be the same. (4) In general, for solutions of equal concentration of the same or different substances in different solvents, the difference in surface tension in each case between solution and solvent should be equal. In each of the above laws allowance is to be made, in the case of electrolytes, for the degree of dissociation.

It is pointed out that solutions of liquids offer the only exceptions to law (1), but that such solutions do not obey the vapor-pressure law either. The work of Quincke[1] and Volkmann[2] on surface tension shows that laws (2) and (4) hold very nearly, while the experimental evidence in regard to law (3) varies.

After a careful comparison of his own results in the surface-tension measurements of a large number of solutions with the osmotic pressures of the same solutions, measured by Overton,[3] Traube[4] states that "among hundreds of combinations.... there is not one in which capillary and osmotic phenomena do not correspond." He arrives at the following conclusions: (1) "The greater the osmotic velocity of a substance soluble in water, the more this substance reduces the capillarity constant of water." (2) "Substances that cannot penetrate membranes (with regard to which the membranes are semipermeable) increase the constant of capillarity of water." (3) "The difference of surface tensions determines the direction and velocity of osmosis," the osmotic flow being always from the region of less to that of greater surface tension. Difference in surface tensions is therefore regarded as "the motive force in osmotic phenomena."

Battelli and Stefanini[5] have called attention to certain cases which do not conform to the rules of Traube. Thus Monte[6] had shown that, although salicin lowers the surface tension of water, when an aqueous solution of this substance and water are separated by a membrane, osmosis takes place in the direction of the solution. Also when ethyl alcohol and water are separated by an animal membrane, the os-

[1] Pogg. Ann., **160**, 337 and 560 (1877).

[2] Wied. Ann., **17**, 353 (1882); **28**, 135 (1886).

[3] Vierteljahresschr. d. Naturf. Ges. (Zurich), **40**, 159 (1895), and **44**, 88 (1899); Z. physik. Chem., **22**, 189 (1897).

[4] Phil. Mag. [6], **8**, 704 (1904); see also Ann. Phys. u. Chem., **62**, 490 (1897).

[5] Physik. Z., **7**, 190 (1906); J. de Phys., **6**, 402 (1907).

[6] Cim. [4], **5**, 186 (1897).

motic flow is in the direction of the alcohol, that is, from the region of greater to that of less surface tension. Battelli and Stefanini find the same is true when alcohol and water are separated by a membrane of nickel ferrocyanide. These authors have attempted to reconcile these and other discrepancies by a slight modification of the idea of Traube. They agree with him in ascribing osmotic phenomena to differences in surface tension on the two sides of the membrane, but according to their view, osmosis will proceed in the direction which lends itself best to an equalization of surface tensions. If the membrane is permeable to but one of the liquids, it alone will pass through; if it is permeable to both, osmosis will take place in both directions, till surface tensions are equalized, but at different rates, depending on the specific nature of the two liquids. Thus if the passage of *n* molecules of water would *increase* the surface tension of the given mass of alcohol less than the passage of *n* molecules of alcohol would *decrease* the surface tension of the water, then the rate of flow of water will be the *more rapid*. In other words, that liquid of which *n* molecules will have the *greater* effect on the surface tension of the other will diffuse more *slowly*.

According to the measurements of Battelli and Stefanini, solutions having equal surface tensions exert the same osmotic pressure regardless of molecular concentration. They found that a 1.78 per cent solution of magnesium sulphate and a 1.11 per cent solution of sodium sulphate have the same surface tension. On placing one of these on the interior and the other on the exterior of an osmotic cell (presumably using a nickel ferrocyanide membrane) no difference of pressure was observed. They experimented in a similar manner with solutions of cane sugar and mannite, copper sulphate and sodium chloride, etc., and always obtained the same result.

The Theories of Poynting and Lowry.

Poynting[1] explains osmotic phenomena on the basis of the formation of labile hydrates, each composed of a molecule of the dissolved substance as a nucleus, surrounded by a number of solvent molecules, the whole forming an unstable complex in which the solvent molecules are constantly changing places. Consider the case of a pure liquid in contact with its vapor. Generally accepted theory postulates a continuous process of evaporation, resulting from molecules striking the surface with sufficient velocity to overcome the attractions of neighboring molecules. This evaporation

[1] Phil. Mag. [5], 42, 289 (1896).

is balanced by the condensation of practically all the vapor particles impinging on the surface. Now in the case of a solution, the solvent molecules included in the complexes alluded to above are not free to pass out into the region of vapor and hence evaporation proceeds more slowly than from the pure solvent, but these complexes are regarded as quite as effective as solvent molecules in entangling vapor particles coming in contact with the surface separating solution and vapor, which surface is semipermeable as regards solute and solvent. Thus condensation would proceed more rapidly than evaporation till equilibrium between the two is established, both the evaporation and condensation proceeding at a lower rate than in the case of the pure solvent. Essentially the same conditions prevail at the surface of contact of a solution and the more conventional semipermeable membrane, the principal difference being that here we have rigidity and consequently any excess of "condensation" over "evaporation" would give rise to a hydrostatic pressure, which is the measure of osmotic pressure.

The theory, when worked out quantitatively and applied to aqueous solutions, leads to the result that substances which are monohydrated should give normal osmotic pressure; substances which unite with two molecules of water should give twice the normal pressure, etc.

Lowry[1] has advanced a conception of osmotic pressure very similar to that of Poynting. Here likewise the retardation of evaporation is brought about by the presence of non-volatile solute molecules in the surface layer, which may or may not, however, be hydrated, the *modus operandi* being slightly different in the two cases. According to Lowry, if a molecule of solvent strikes one of these solute molecules in the surface layer, it rebounds and is thus prevented from passing into the region of vapor, while condensation proceeds here also as if no solute were present.

The quantitative application of the theory of Lowry follows directly from the relation between osmotic pressure and vapor pressure as worked out by Nernst[2] and, unlike that of Poynting, within certain limits seems to be independent of the complexity of the hydrates formed.

Sutherland's View.

Sutherland[3] offers an explanation of the mechanism of the entrance of solvent into an osmotic cell on the basis of

[1] Trans. Faraday Soc., 3, 12 (1907); Phil. Mag. [6], 13, 552 (1907).
[2] Theoretical Chemistry, pp. 124-129.
[3] Phil. Mag. [5], 44, 493 (1897).

the sievelike action of the membrane. He conceives of the membrane as containing "meshes" large enough to permit the passage of solvent more or less freely while the dissolved molecules are effectually held back. If we assume such a semipermeable membrane separating water and a dilute solution of cane sugar, the sugar molecules, impinging on the "quasi-solid framework" of the membrane, give rise to the pressure just as the impacts of the molecules cause pressure in gases. The laws governing this pressure are the same as in gases, since the phenomena are essentially the same. Consider a membrane with pure water on both sides. The molecules of water in the pores are subject to impacts from other molecules coming from all directions, very much as if no membrane were present. If now we substitute a sugar solution on one side of the membrane, "the sugar molecules are to be regarded as replacing some water molecules, but their collisions on the water in the membrane are rendered inoperative by the shielding action of the framework so that the water molecules in the membrane receive more impacts on the side of the pure water than on the side of the solution and therefore water flows through the membrane" till the excess of hydrostatic pressure on the solution side compensates for the inoperative impacts of the sugar molecules.

A similar mechanical view of Pickering[1] rests on the supposed greater ease with which solvent complexes dissociate, as compared with hydrates in solution. The membrane is supposed to be impermeable to these hydrates and possibly to the larger molecular aggregates in the pure solvent, but permeable to simple water molecules or even to the smaller aggregates.

The "Solution" Theory.

This theory is in substance the following: Given a membrane separating two miscible liquids, *A* and *B*, and suppose *A* to be "soluble" in the membrane or, in other words, that the membrane has the power to absorb *A*, while *B* is not soluble. Under these conditions *A* will dissolve in the membrane on the one side and be given up to *B* on the other. If the liquid *B* is in a closed cell, the transfer of *A* will continue till a definite hydrostatic pressure is developed, the magnitude of which depends on the relative attractions of *B* and the membrane for *A* and probably also on the temperature. The action of a copper ferrocyanide membrane separating water from an aqueous solution of cane sugar, for example, depends on the solubility of water and the insolubility of

[1] Ber. d. chem. Ges., **24**, 3629 (1891).

the sugar or the sugar solution, so that the membrane becomes saturated with water with respect to the solvent on the one side, while it is supersaturated with respect to the solution on the other. Hence there is a transfer of solvent across the membrane till the hydrostatic pressure developed becomes sufficient to check the flow.

L'Hermite[1] appears to have been the first to state clearly the view that osmotic phenomena in general are due to this "selective action" of the membrane. According to him endosmose depends on two conditions: (1) The two liquids must be miscible, and (2) one of the liquids at least must be soluble in the membrane. He described a number of "three liquid-layer" experiments which he regarded as typical of osmotic processes in general. For example, he disposed, in a cylinder, layers of ether and chloroform separated by a layer of water and observed that the ether gradually dissolved in the water, to be abstracted, in turn, by the chloroform. By suitable arrangements he was able to show that such transfer resulted in the development of a not inconsiderable pressure.

Kahlenberg[2] in recent years has furnished a considerable amount of evidence in support of this view. He has carried out a large number of experiments on the osmotic pressures of solutions of various kinds, using membranes of rubber and parchment, and has arrived at the following conclusions: (1) Osmosis, both in direction and extent, depends on the specific nature of the membrane used and of the liquids that bathe it; that is, on the "selective action" of the membrane. (2) That the gas laws do not hold for solutions in general. Any agreement between the osmotic pressure of solutions of cane sugar, glucose, etc., and the elastic pressure of gases he would regard as purely fortuitous. (3) Deductions of the thermodynamicist, based on the assumption of a semipermeable membrane, are valueless and misleading, since a perfectly semipermeable membrane is experimentally impossible.

Armstrong's Theory.

Prof. Armstrong[3] explains osmotic and related phenomena on an association, rather than a dissociation, hypothesis. All liquids are regarded as in some degree associated. In water, for example, we have probably both simple and poly-

[1] Ann. Chim. Phys. [3], 43, 420 (1855); Compt. rend., 39, 1177 (1854).

[2] J. Physic. Chem., 10, 141 (1906). See also Trans. Faraday Soc., 3, 23 (1907) and various articles in Nature.

[3] P. Roy. Soc. [A], 78, 264 (1906).

merized molecules, in equilibrium, represented thus: $(H_2O)_n \rightleftarrows nH_2O$. The addition of a nonelectrolyte involves a disturbance of equilibrium in the direction $(H_2O)_n \longrightarrow nH_2O$. These monads are regarded as exerting an attraction for similar molecules in the region of pure solvent or of a more dilute solution. There will accordingly be a transfer of solvent across the membrane till equilibrium is reëstablished, the osmotic attraction, in the case of a nonelectrolyte, being due wholly to the influence of the dissociated water complexes.

Electrolytes, besides producing this dissociation effect, are supposed also to exert an additional attractive influence on the solvent molecules and therefore show a greater osmotic pressure than equivalent molecular concentrations of nonelectrolytes.

In concluding this review, it may be said that those who hold to the thermodynamic explanation of osmotic phenomena do not regard it as necessarily excluding the views which are concerned primarily with the mechanism by which the solvent enters the cell, such as the "solution theory," advocated by Kahlenberg. Findlay[1] states that "in thermodynamics, they did not consider at all how the membrane acts, provided the changes in energy were equal in opposite directions." Whetham[2] says that "it is the strength of thermodynamic reasoning that it avoids the uncertainties of definite hypotheses about the mechanism of the connection between the two series of phenomena it correlates; it is the weakness of thermodynamic reasoning that it fails to throw light on the ultimate structure of the system which such hypotheses seek to examine." And hence, although van't Hoff, in his original paper, attributed osmotic pressure to the bombardment of the membrane by the molecules of the dissolved substance, the validity of his deductions is not dependent upon the correctness of this hypothesis. As Whetham remarks,[3] the pressure "may be due to molecular impacts, or to chemical affinity, or to some other undiscovered cause."

B. F. LOVELACE.

JOHNS HOPKINS UNIVERSITY,
March 2, 1908.

[1] Trans. Faraday Soc., 3, 30 (1907).
[2] *Ibid.*, 3, 34 (1907).
[3] Nature, 74, 54 (1906).

THE DEGRADATION OF THE ELEMENTS.

A short paper[1] of unusual significance, bearing the above title, has recently been published by Sir William Ramsay. In this communication there is discussed all that is known in reference to the production of one elementary form of matter from another.

Ramsay starts out with the proposition that[2] "every scientific discovery is a function of two conditions—the concentration of a certain quantity of energy in a small volume, and the possibility of directing this energy to a given end."

He points out that the greatest concentration of energy with which we are familiar is in the radium emanation. A given volume of the emanation will give out *two and a half million times as much heat* as would be set free by the union of hydrogen and oxygen in an equal volume of detonating gas, and this is one of the most exothermic of chemical reactions. It is thus obvious that there is no comparison between the amount of intrinsic energy contained in the radium emanation and that present in the most active chemical elements—the ratio being as millions to one.

The radium emanation is a gas, having a molecular weight of probably about 200. It is unstable, undergoing decomposition spontaneously, yielding the element helium. Like argon, helium, neon, etc., it resists the action of all chemical reagents and is placed by Ramsay with the noble gases:

Noble gases	He	Ne	Ar	Kr	Xe	Emanation
Atomic weights	4	20	39.9	81.8	128	200—216.5

The most interesting and suggestive part of Ramsay's paper may be reviewed as follows: The emanation, as we have seen, undergoes decomposition spontaneously, giving among other things the element helium. If the emanation is allowed to stand in the presence of water, the water is decomposed into its elements, but not in the ratio in which they occur in water. There is always an excess of hydrogen—about 5.5 per cent on an average, the excess of hydrogen varying in a series of nine determinations from 3.65 to 16 per cent.

Under these conditions the emanation produces only traces of helium, *neon* being formed in appreciable quantity. Ramsay interprets these facts in the following manner: Much of the energy in the emanation is expended in doing the work necessary to decompose water, and the emanation itself is not "degraded" to its lowest term, helium, but the degrada-

[1] J. Chim. Phys., 5, 647 (1907).
[2] *Loc. cit.*, p. 647.

tion stops at the second member, neon, with an atomic weight of 20.

Finally, allow the emanation to act on a salt of copper. According to Ramsay there is formed not only sodium, but a trace of lithium. The gas produced is not helium, not neon, but *argon*.

The interpretation here is analogous to that given above, where the emanation is allowed to decompose water. The intrinsic energy of the emanation is expended to a greater extent in doing the larger amount of work required to "degrade" the copper, and, consequently, a smaller amount remains to degrade the emanation itself. The result is that the emanation, under these conditions, does not yield helium, does not yield neon, but argon which has a larger atomic mass.

Ramsay concludes by stating that in the gas which is given off spontaneously from a solution of thorium nitrate, he finds carbon dioxide. He points out that carbon is the first member of the natural family of which thorium has the largest atomic weight.

He raises the question as to whether the carbon may not be produced as the result of the degradation of the thorium by the intrinsic energy in the latter, which, as we know, is also radioactive. H. C. J.

REVIEWS.

COMMERCIAL ORGANIC ANALYSIS. A Treatise on the Properties, Modes of Assaying, and Proximate Analytical Examination of the Various Organic Chemicals and Products Employed in the Arts, Manufactures, Medicines, Etc. By ALFRED H. ALLEN. Volume II., Part 3, Third Edition. Rewritten and revised by the Author and ARNOLD RAMSBY TANKARD. Philadelphia: P. Blakiston's Sons & Co. 1907. pp. xii + 547. Price, $5.

The appearance of this new edition of Part 3 completes the third edition of Volume II. of this helpful and extensive treatise on Commercial Organic Analysis. The first portion of the volume is devoted to the aromatic acids, the subject matter being greatly amplified as compared with the second edition. But the distinctive mark of the volume is the thorough discussion of resins and essential oils, in keeping with the great advances made in this field during recent years. The four hundred pages given to these last subjects are a striking contrast to the scant twenty-five pages of the first edition. It is a matter for congratulation that

this mass of material, widely scattered through chemical literature, has been assembled in concise and attractive form. And it is not a mere compilation of analytical methods, for each subject is headed by a brief theoretical discussion which makes the volume instructive reading. Frequent tables, summarizing the properties of related compounds, add to its convenience as a laboratory reference book. References to the literature are to be found on practically every page, but it is to be regretted that this feature has not been made complete.

Where there is so much to be commended, it seems scarcely just to criticize minor errors, and yet there are a number of these which indicate carelessness. To one not familiar with the literature of the subject, the incorrect "Mauch" on pages 146 and 148, with no reference given, is apt to be confusing in view of the correct spelling "Mach" on pages 159 and 160. The expression (page 165) "is boiled with 50 cc. of alcoholic potash" leaves no room for doubt as to volume, but it is indefinite as to concentration. The description (page 142) of Tschirch's method for the proximate analysis of resinous substances is erroneous in that Tschirch, after separation of the resin acids, removes the ether, *then* subjects the residue to steam distillation. The opinion of the authors (page 146) that two carboxyl groups appear to exist in the molecule of abietic acid is flatly contradicted on page 160 by the sentence "Abietic acid is frequently described as dibasic but the presence of only one carboxyl group in the molecule and the proportion of alkali required for its neutralization conclusively negatives this view." On page 161, the unsaponifiable portion of colophony (resene) is stated probably to "consist chiefly of hydrocarbons of the nature of resin oil, produced by the action of heat on the colophony during the process of manufacture." In this view, the authors are evidently following Fahrion. But this probability rapidly changes to improbability if we accept the work of Tschirch, who finds an even higher percentage of this unsaponifiable matter (resene) in the oleo-resin from which colophony is manufactured. In the footnote on page 157 the assertion is made that "the resin from a given tree also becomes darker year after year." Abundant demonstration has been made that this increasing coloration of the resin is due solely to the method of collecting the crude turpentine from which the resin is obtained. Collected under similar conditions in succeeding years of operation, no change in the color of the resin can be detected. The first paragraph of the section on "Common Turpentine,"

page 196, is so filled with errors that it should be entirely rewritten.

These criticisms, however, are on minor points and do not affect the great value of the work as a most helpful laboratory guide in a difficult subject. CHAS. H. HERTY.

MERCK'S 1907 INDEX (Third Edition). An Encyclopedia for the Chemist, Pharmacist, and Physician, Stating the Names and Synonyms; Source or Origin; Chemical Nature and Formulas; Physical Form, Appearance and Properties, Melting and Boiling Points; Solubilities; Specific Gravities and Methods of Testing; Physical Effects; Therapeutic Uses; Modes of Administration and Application; Ordinary and Maximum Doses; Incompatibles; Antidotes; Special Cautions; Hints on Keeping and Handling, Etc., of the Chemicals and Drugs used in Chemistry, Medicine and the Arts. New York, St. Louis, Mo., Rahway, N. J.: Merck & Co.

The title page shows clearly what this publication is intended for. It will be found very useful as a book of reference, especially in these days when the chemist finds it extremely difficult to keep abreast of the times in the flood of new remedies with meaningless names. It contains a vast amount of valuable information so presented that anything wanted can readily be found.

UEBUNGSBEISPIELE AUS DER ANORGANISCHEN EXPERIMENTALCHEMIE. Von HEINRICH BILTZ und WILHELM BILTZ. Mit 26 Textfiguren. Leipzig: Wilhelm Engelmann. 1907. pp. 232. Price, 7 M.

At first sight this book would be considered simply a manual of inorganic preparations, containing many familiar preparations, and many not usually included in such manuals, among which may be noted elements obtained by Goldschmidt's method of reduction by aluminium, colloidal elements, salts of complex acids, and a number of metal-ammonium salts. The book closes with a chapter on the preparation of compounds of the rare earths from minerals.

A closer examination shows many experiments designed to illustrate physical-chemical laws and methods, and a series of well written introductions to the several sections of the book, in which the writers discuss recent theories and methods. For example, in the chapter on the salts of halogeno-acids (such as silicofluorides) and on complex cyanogen compounds (such as potassium cobalticyanide) the authors refer to the work of Abegg, to Bodländer's measurements of the stability constants of the complex anions containing metal, and to Werner's theory of primary and secondary valence (Neben-Valenzen) to explain the structure of this type of compounds.

From what has been said it is evident that this is not a book for beginners, indeed the writers say so in their preface. It would be a most valuable book for American post-graduate students, and teachers of inorganic chemistry will find it interesting and useful to select work for their students, as most of the preparations are not too difficult for an undergraduate student who has had some practice in preparation work.

E. R.